THE PROCEEDINGS OF
THE PHYSICAL SOCIETY

VOL. 45, PART 2 *March* 1, 1933 NO. 247

621.317.755

TIME-MARKING A CATHODE-RAY OSCILLOGRAM

BY LEWIS F. RICHARDSON, F.R.S.

Received August 2, 1932. *Read December* 2, 1932.

ABSTRACT. Time-marks have been arranged as little blurs or gaps in the trace, by periodically unfocusing the electron stream. The current in and voltage across a conductor can thus be recorded simultaneously with the time on a single oscillogram.

ALTHOUGH excellent arrangements for recording the time on an oscillogram are already available, such as the linear time-base used by Appleton, Watson Watt and Herd* combined with the trigger of Finch, Sutton and Tooke†, yet these give the time as one co-ordinate and so leave only one co-ordinate for the phenomenon to be investigated. There is an obvious need for a different method, now to be described, having the advantage that both co-ordinates are allocated to the phenomena, say one co-ordinate for voltage, the other for current. It would be possible to distort the trace by an impressed ripple. In particular D. W. Dye‡ has shown how to apply a small deflection either parallel to a fixed direction or radial or circular. But ripples are not satisfactory for two reasons: (i) the distortion hinders measurement; (ii) the ripple is invisible where its displacement is parallel to the undisturbed trace. Instead, time-marks at intervals of 10^{-3} or 10^{-4} sec. have been arranged as little blurs or gaps in a trace otherwise undistorted.

In recent types of oscillograph (I have used that of Standard Telephones and Cables Ltd.) the spot is focussed by applying a suitable potential to a cylindrical shield surrounding the filament. The time-marks have been made by unfocusing the spot at regular short intervals of time, by applying to the shield a periodically varying potential generated by a triode oscillator of an ordinary kind§.

---

* *Proc. R. S.* A, **111**, 672 (1926).

† *Proc. Phys. Soc.* **43**, 502 (1931).

‡ *National Physical Laboratory; Report for the year* 1924, pp. 77, 78.

§ Like figure 177 of L. B. Turner's *Wireless*, p. 267 (Camb. Univ. Press, 1931).

The appearances are shown in oscillograms 1, 2, 3, 4, in all of which the two co-ordinates of the phenomenon depend severally on the voltage and current in a condenser supplied with a.c. at 50 ~ from the town mains.

The tuning capacitance of the time-marker was placed close to the oscillograph so that the observer could vary the frequency of the time-marks while watching the oscillograph trace. But the tuning inductance was put 5 metres away to avoid its stray field.

The effects of mistuning are like those seen on a stroboscope. For example suppose that by means of a frequency, known to be about 20 times that of the mains, 20 stationary time-marks appear on the orbit of the light-spot; and that the tuning capacitance of the time-marker is then gradually decreased until 21 stationary marks appear. During this passage various appearances are seen: time-marks hurrying to and fro, and blurred stationary patterns of about $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, ... of the spacing characteristic of the 20th harmonic. It is easy to recognize these intermediate patterns by their closeness and by their blurring, and so to avoid them. They have been avoided in the present work.

To decide which way the light-spot was moving, the following experiment was made. The tuning capacitance of the time-marker was set to give stationary harmonic marks. The capacitance was then suddenly increased by a small fraction of the change that would produce the next lower harmonic. This caused the time-marks to move along the trace in the same sense as the light-spot. Thus we can put the head on time's arrow.

Some puzzling oscillograms concerning neon-lamps were resolved by the aid of slowly moving time-marks. A piece of trace that had appeared to be single was seen to be traversed by two sets of time-marks moving opposite ways.

The following three propositions have been found very serviceable in the interpretation of oscillograms:

I. The speed of the moving time-marks is the same fraction of the speed of the light-spot in all parts of its trace.

II. When the marks are stationary, a sudden increase of the tuning capacitance by one five-hundredth of its effective amount, including self-capacitance, causes the marks to advance with one-thousandth* of the speed of the light-spot.

III. The separation of sufficiently close time-marks is to their speed in a ratio which is the same for all parts of the trace.

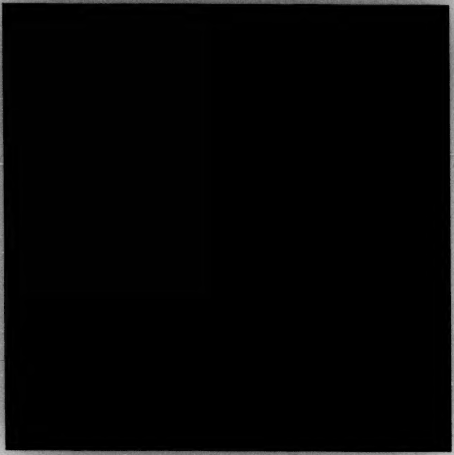
Proofs of these propositions are given in the Appendix.

As this scheme has been tried out in various special forms, some of which gave neat definite gaps in the trace while others gave blurred patches too vague for accurate measurement, it may be desirable to describe the arrangements in more detail.

Figure 1 shows a simple connexion. On the left F is the filament, S the shield, and A the anode of the oscillograph. The focus is adjusted by the voltage B of the

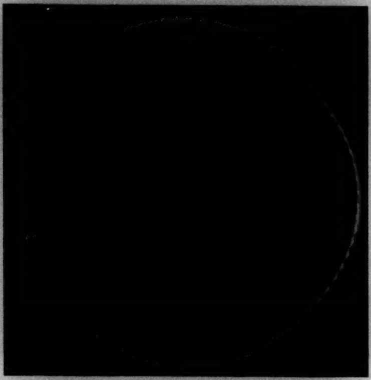
---

* More accurately 1/1001. [Note added December 3, 1932.]

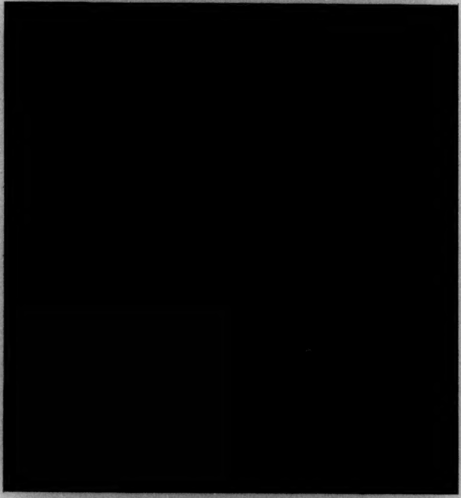


No. 1. 50 × 20 marks per second. Circuit of figure 1.

No. 2. 50 × 20 marks per second. Circuit of figure 2; $W \to \infty$, $R = 0{\cdot}28\,\mathrm{M}\Omega$., $M = 129$ V., $K = 50\,\mu\mu\mathrm{F}$.



No. 3. 50 × 86 marks per second. Circuit rather like that of figure 2. Undesirable ripple.



No. 4. 50 × 107 marks per second. Circuit of figure 1. Separate beads, easily counted.

battery. There was a range of about 12 volts over which the focus was moderately good; so the oscillating voltage supplied by the coil L had to be of this order. If B were set for the middle of the range of fair focus and the amplitude ϕ of the time-marking oscillation were large enough, we should expect a blur for every half wave. Actually ϕ was usually too small for that, so B was set near one end of the range, making only one blur in each whole wave. For example in oscillogram No. 1, the phenomenon had a period of 0·02 sec., the time-marker a period of 0·001 sec., and there are 20, not 40, gaps.

It is an advantage to have the resistance R adjustable between 10^4 and $10^7\ \Omega$, for by its aid the conspicuousness of the time-marks is easily controlled. The trade-name of the resistance was "power-clarostat, universal range."

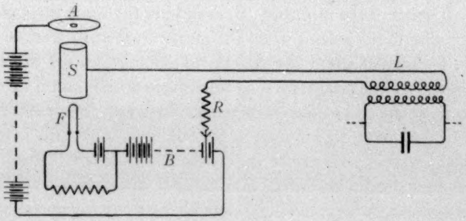


Figure 1.

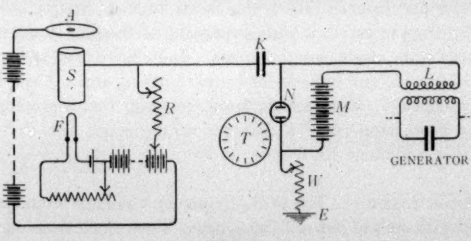


Figure 2.

In oscillogram No. 1 the gaps are too large and the trace near the gaps too distorted. The circuit of figure 2 gave better results.

Here N was a neon (osglim) lamp to make sudden jerks of potential by lighting 10^3 times per second. As the oscillator alone did not give enough volts to flash the lamp, the battery M was added. But even so the range from maximum to minimum given by the coil L had to exceed some 40 volts in order both to light and extinguish the lamp. The function of the capacitance K of about $0{\cdot}001\mu$F is to transmit the jerk but to insulate for steady currents. If the potential at one side of N be steadied by shorting W to earth, the jerk of potential will all come on the other side of N.

When this was tried, the oscillograph emitted a note of the frequency of the time-marker, and lest the filament should be broken, the circuit was hastily disconnected. But a moderate resistance W might be helpful. As the jerk at the lighting of the osglim only lasts about 10^{-5} sec., it seemed desirable to treat the connexion from N to S in the manner customary for radio-frequency, taking care to avoid stray capacitances to earth and removing the choke-coil which the makers put in the cap of the osglim. No protective coil was needed, as the power supplied by L was insufficient to cause arcing. Oscillogram No. 2 was marked by the circuit of figure 2. It is seen that the marks are definite to 3×10^{-5} sec.

Photography was difficult because the marks were seldom still for 3 seconds continuously. Their random to-and-fro motion along the trace was presumably due to variations in the frequency of the Paisley town mains; and this disturbance was less in the small hours of the morning. By watching the trace through a magnifying glass and beginning the exposure when the marks were still, relative to the crystals on the screen, I obtained about one successful photograph for five exposures. By a fortunate chance a cinematograph lens was found which had a field curved so as approximately to fit the end of the oscillograph like a cap. The curvature was therefore opposite to that given by a simple bi-convex lens. This lens is marked "$3\frac{1}{2}$ in. Paragon Special," and is a variety of the Petzeval objective*. Ilford "Golden Iso-Zenith" plates were used with satisfaction. Almost confluent marks on the negative were sometimes separated by making a contact print on a process plate.

Standards of frequency. The triode oscillator kept a frequency sufficiently steady for photography; for as tested by beats against a vibrating steel bar, its frequency varied only by 1 part in 2000 during the course of an evening. But variations of several per cent from month to month, depending on the filament-temperature and on the potentials of the anode and grid, made it desirable to refer to better standards. These are well known, and include for instance tuning-forks, Campbell hummer-bars and wave-meters†. But perhaps I may mention that a gramophone, a protractor and a neon lamp make a domestic stroboscope; also that a water-tube resonator with a telephone fixed near its mouth is a cheap and convenient instrument.

Peculiarities at 10,000 ~. The audio-frequency oscillator would not go so high until provided with coils of less self-capacitance. Then small time-marks got across mysteriously from oscillator to oscillograph even when there was no wire connexion. These marks however were not of much use, because they were small displacements of the trace all parallel to one direction and therefore invisible for those parts of the trace that went in that direction when unmarked. The circuit of figure 1 provided proper time-marks visible in all parts of the trace. The circuit of figure 2 did not succeed any better, owing to insufficient voltage to flash and extinguish the osglim lamp.

---

* J. W. French, *Dict. App. Phys.* **4**, 158.

† D. W. Dye, "Radio-frequency Measurements," *Dict. App. Phys.*

Example of an observation to standardize a wave-meter:

Time of day a.m.	All capacitances mentioned below were those of the generator; and $C = 0{\cdot}066_0\,\mu$F.
2.55	Stroboscope of 100 holes illuminated by neon lamp at the town's frequency, 100 revolutions in $100{\cdot}1_0$ sec.
2.59	Wave-meter maximum resonance at $C + 0{\cdot}00036$
3.10	Photograph of oscillogram at $C + 0{\cdot}00016$
3.15	Wave-meter maximum at $C + 0{\cdot}00027_5$
3.20	Stroboscope as above, in $100{\cdot}0_6$ sec.
3.30	A correction for the effect of the galvanometer lamp on the filament-current of the generator was easily determined by holding the same harmonic pattern of time-marks steady on the oscillogram while switching the lamp on and off. It was found that the capacitance at the time of the photograph should be increased to $C + 0{\cdot}00036$, leaving the other capacitances as stated

The change of frequency ν with capacitance C, although given roughly by $\nu = 1/2\pi\sqrt{(LC)}$, is easily and more accurately determined by suddenly turning the knob of an air condenser so as to pass from the photographed harmonic pattern to the next, a change of 50 ~. In this way it was found that 50 ~ corresponded to $0{\cdot}00059\,\mu$F. On projecting the photograph to form an image 44 cm. in diameter it was just possible to count the time-marks. There were 196 of them.

The frequency of the wave-meter was accordingly calculated thus:

$$\frac{100 \times 100}{100{\cdot}1_0 + 100{\cdot}0_6} \times 196 - \left(\frac{36 + 27{\cdot}5}{2} - 36\right)\frac{50}{59} = 9792 + 4 = (9796 \pm 10) \sim,$$

an absolute determination. Another set of observations gave 9801 ~. The separation of these marks is about equal to the diameter of the light-spot, so that closer marks could hardly be resolved and there is little prospect of counting 400 time-marks on a single oscillogram.

ACKNOWLEDGMENT

The Government Grant Committee of the Royal Society provided some apparatus, which has been a great help.

APPENDIX

Proofs of theorems

Let T denote the time taken by the light-spot to make each circuit of its trace. T

Let $(T + \epsilon)/n$ denote the interval of time between successive time-marks; and let n be an integer. ϵ, n

If $\epsilon = 0$ the marks are stationary. Let us ignore in this theory those rather blurred stationary marks for which n is an integer plus a simple fraction such as $\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$; for it has been shown how to observe and reject such marks experimentally.

The arcual distance S_1 between two successive stationary marks is travelled by the light-spot in a time T/n. So if V_1 denote the mean speed of the light-spot for that part of its course, S_1 V_1

$$TV_1 = nS_1 \qquad \text{......(1).}$$

S U

But if $\epsilon > 0$, consider any time-mark. Call it the zeroth mark occurring at time zero. The light-spot returns to the same point on the screen at the time T. But the nth mark has not yet arrived and so the light-spot moves on through a further distance S, say, to where the nth mark occurs at the time $T + \epsilon$. If S is a small fraction of the distance between successive marks, we see an apparent forward motion, familiar on the stroboscope. Let U be the speed of this apparent motion. It is due to an advance S during the time between the zeroth and the nth mark. This time-interval is $T + \epsilon$. So

$$S = U(T + \epsilon) \qquad \ldots\ldots(2).$$

V

Let V denote the speed of the light-spot for the arc S. Then

$$S = V . \epsilon \qquad \ldots\ldots(3).$$

Here S is so small that V is indistinguishable from the *instantaneous* speed of the light-spot.

Eliminating S between (2) and (3),

$$U = V \frac{\epsilon}{T + \epsilon} \qquad \ldots\ldots(4).$$

Now $\epsilon/(T + \epsilon)$ is independent of position on the trace and so theorem I on page 136 follows.

dC

Next suppose that when the marks are stationary ($\epsilon = 0$) we suddenly increase the tuning capacitance C of the time-marker by an amount dC so that dC/C is small. Assuming for simplicity that the period P of the time-marker is given by the usual formula

$$P = 2\pi \{L(C + \gamma)\}^{\frac{1}{2}} \qquad \ldots\ldots(5),$$

L, γ

in which L is the fixed tuning inductance and γ its self-capacitance. Differentiating (5) logarithmically, we have

$$\frac{dP}{P} = \frac{1}{2} \frac{dC}{C + \gamma} \qquad \ldots\ldots(6).$$

But

$$\frac{dP}{P} = \left(\frac{T + \epsilon}{n} - \frac{T}{n}\right) \Big/ \left(\frac{T}{n}\right) = \frac{\epsilon}{T} \qquad \ldots\ldots(7).$$

Eliminating dP/P between (6) and (7) and inserting the result in (4),

$$U = V \frac{dC}{2(C + \gamma) + dC} \qquad \ldots\ldots(8)^*,$$

which includes theorem II.

To prove theorem III we compare equation (1) with equation (4), obtaining

$$S_1 = \frac{T}{n} V_1 = \frac{T}{n} V . \frac{V_1}{V} = \frac{T}{n} U \left(\frac{T + \epsilon}{\epsilon}\right) \frac{V_1}{V} \qquad \ldots\ldots(9).$$

Now as $n \to \infty$, $V_1/V \to 1$, leaving

$$S_1 = U . T \frac{T + \epsilon}{\epsilon n} \qquad \ldots\ldots(10),$$

---

[*] Revised December 3, 1932.

and although we cannot make n approach ∞ in the experiments, yet we can usually make n large enough for (10) to be an excellent approximation. The factor $T(T+\epsilon)/\epsilon n$ is independent of position on the oscillogram; whence theorem III.

DISCUSSION

Prof. G. I. Finch. The trace-luminosity afforded by a medium-speed electron beam focussed by a Wehnelt cylinder is often so low that the phenomenon under observation must be repeated many times in order to obtain a photographic record. The value of Dr Richardson's neat and useful method of time-marking would therefore be greatly enhanced if means could be found of locking time-marking and trace together in such a manner that the time-marks coincided accurately throughout a large number of repeated traces.

Author's reply. Thinking of the work of Finch, Sutton and Tooke on synchronization I made many attempts to use a continuous method of synchronization, namely to take as the time-marker a high harmonic of the trace-frequency. The harmonic was produced by a copper-oxide rectifier and picked out by a resonant triode circuit. This scheme succeeded with the lower harmonics such as the 10th, but was no use at all with the higher harmonics such as the 200th.

532.13:541.182.62

THE FLOW OF LIQUID SUSPENSIONS

By E. G. RICHARDSON, B.A., Ph.D., D.Sc.
AND
E. TYLER, D.Sc., F.Inst.P.

Received October 13, 1932. *Read December* 16, 1932.

ABSTRACT. Measurements of the velocity from point to point in a liquid rotating in the space between two concentric cylinders, of which the outer rotates while the inner is still, are made by means of a hot-wire anemometer. It is shown that in a suspension the velocity-gradients are abnormal but can be explained in terms of a variable viscosity, which is a function of the velocity-gradient.

---

§ 1. INTRODUCTION

The anomalous viscosity of disperse systems has become a common subject of research in recent years. As soon as liquid suspensions and gels were investigated in viscometers of either the capillary-flow or the concentric-cylinder type, it was found that the coefficient of viscosity was not a constant for a given liquid; for instance, that in the capillary-flow apparatus the pressure-gradient increased less rapidly than the outflow it produced, or, that in the concentric-cylinder apparatus the velocity of the outer rotating cylinder increased more rapidly than the torque it produced on the inner. It was, in fact, impossible to measure the viscosity absolutely, the measured value being dependent on the apparatus and the conditions under which it was used. In order to obtain data for comparing the behaviour of such systems with that of ordinary liquids, it is necessary, as Hatschek* points out, to measure the velocity from point to point across the liquid, and to compare velocity-gradients.

Two attempts in this direction have recently been made, both with a flow apparatus and with a gelatine solution. Kroepelin† traversed a Pitot tube across the end of the flow tube at the place where it debouched upon the outflow reservoir, and obtained curves of velocity transverse to the flow, showing small departures from the Poiseuille (parabolic) distribution. The sol was a gelatine solution. Pichot and Dupin‡ used a fluid partaking of both suspension and sol characteristics, consisting as it did of a 7 per cent solution of gelatine in water, with aluminium particles to make visible the relative velocities of different parts when an exposure was made. From the two photographs given (water and gelatine solution respectively) it is difficult to detect any considerable difference in the behaviours of homogeneous and heterogeneous liquids. We have found that gelatine is very difficult to work with, owing to the gradual change in its properties which occurs during an experiment.

* *Viscosity of Liquids*, bibliography given on p. 227 (1928).
† *Z. f. phys. chem.* **149**, 291 (1930).
‡ *Comptes Rendus*, **192**, 1079 (1931).

§ 2. EXPERIMENTAL ARRANGEMENTS

The hot-wire anemometer can readily be adapted to measurements in liquids*; there is however a smaller change of resistance with velocity of the liquid than when the same wire is used under the same conditions in air.

In the present research a vertical wire of nickel, 0·001 in. in diameter, was used. It was heated by a current of 0·30 A. and was calibrated by being mounted on a small whirling arm which carried it in a circular path, 42 cm. in diameter, through the liquid contained in an annular tank. The resistance of the wire was measured in a Kelvin bridge circuit for various speeds of revolution of the whirling arm, an allowance being made for the drift of the fluid in the tank. Typical calibration curves are shown on figure 1.

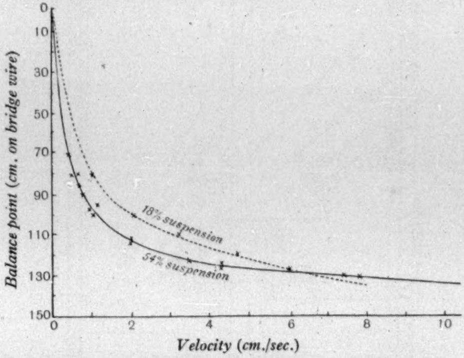


Figure 1. Calibration curves for hot-wire anemometer.

Before applying these curves, another test is necessary. When the wire is used in close proximity to a solid surface, e.g. the walls of the vessel containing the fluid in motion, there is a loss of heat due to conduction across the thin film of fluid between the wire and the surface. This is additional to the heat-loss by convection due to the moving fluid. In this case, it was found, by moving the wire towards the outer cylinder while the liquid inside was still, that the resulting decrease of resistance did not arise until the wire was within 0·5 mm. of the brass surface. As all measurements of flow were made outside this distance, it was unnecessary to apply a correction.

The actual apparatus for the viscosity and velocity gradients was of the Couette type, and is drawn in figure 2; it had been previously used in a slightly different form by one of us† for measurements in homogeneous liquids. The hot wire *W*, 1·5 cm. long, is carried vertically on the ends of two fine needles inserted through ebonite bushes in the outer brass cylinder, which is rotated by the pulley *P* below. Electrical connexion to the fork blades is assured by dippers working in the fixed annular rings of mercury *GG* mounted below the fork. The speed of this cylinder is observed by means of a neon lamp *N* illuminating the stroboscopic disc *D*, and the flashing of the lamp is controlled by a vibrating reed of standardized frequency.

---

* Davis, *Phil. Mag.* **40**, 692 (1920) *et seq.*

† *J. Sci. Inst.* **6**, 337 (1929).

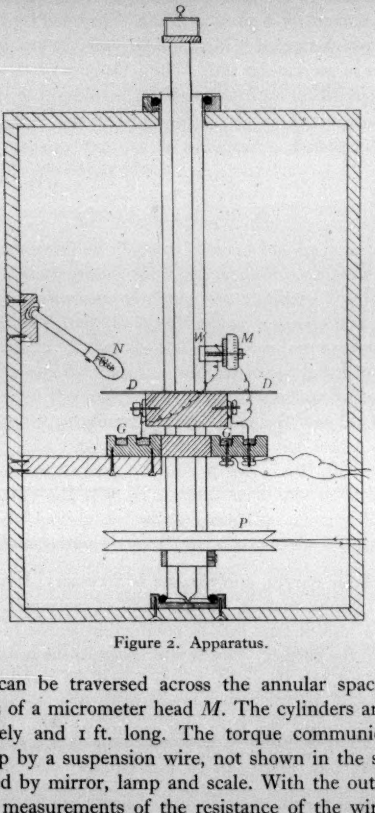


Figure 2. Apparatus.

The hot wire can be traversed across the annular space between the two cylinders by means of a micrometer head *M*. The cylinders are 1 in. and $\frac{1}{2}$ in. in diameter respectively and 1 ft. long. The torque communicated to the inner cylinder is taken up by a suspension wire, not shown in the sketch, the twist on which was indicated by mirror, lamp and scale. With the outer cylinder rotating at constant speed, measurements of the resistance of the wire at various points across the inter-cylindrical space were made, and these were converted into relative velocities by the use of the appropriate calibration curve. Figure 3 shows a set of velocity-distribution curves for paraffin. These are nearly linear, in accordance with theory. Figure 4 shows graphs of torque (in cm. of scale deflection) against velocity of outer cylinder, similar to those by which anomalous viscosity was first indicated.

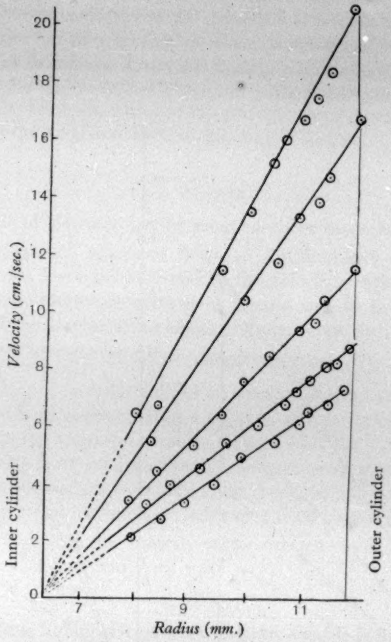


Figure 3. Velocity-gradients in paraffin.

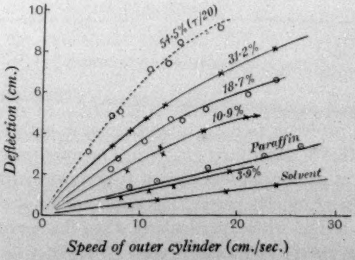


Figure 4. Variation of torque with speed of outer cylinder. The ordinates for the top curve have been reduced to $\frac{1}{20}$.

The paraffin shows, of course, constant viscosity (torque proportional to rate of shear), but the suspensions, with the exception of the weakest, all show diminishing viscosity as the rate of shear is increased. These suspensions were of rice starch in carbon tetrachloride and paraffin, made up according to the recipe of Humphrey and Hatschek[*] as follows: finely ground rice starch was heated carefully in a steam oven for 2 or 3 hours, then passed through a fine sieve and allowed to cool. The suspension was then made up to the required strength with a mixture of paraffin and carbon tetrachloride of density 1·5 gm./cm.^{3} The most concentrated suspension had the consistency of paste, and was chosen to compare with the measurements of Keen and Scott Blair[†] on clay pastes. The outer annuli of this paste rotate with the outer cylinder as a rigid whole, particularly when the speed of the latter is low.

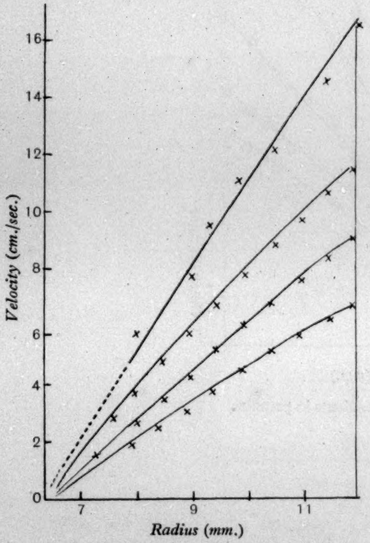


Figure 5. Velocity-gradients in 3·9-per-cent suspension.

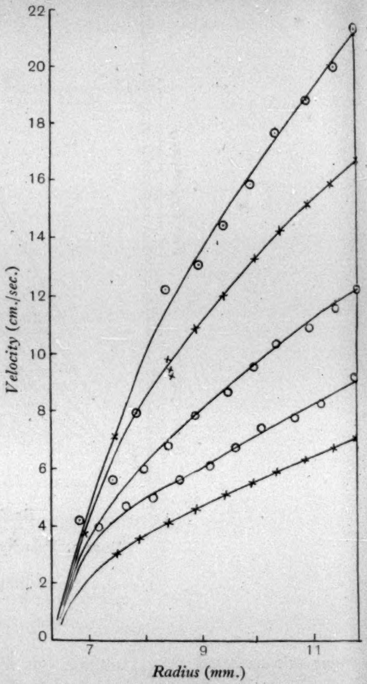


Figure 6. Velocity-gradients in 10·9-per-cent suspension.

---

[*] *Proc. Phys. Soc.* **28**, 276 (1916). We wish to thank Mr Hatschek for the recommendation to use these suspensions on account of their stability.

[†] *J. Agric. Soc.* **19**, 684 (1929).

In no case was the critical velocity for turbulent flow exceeded, although there was difficulty in obtaining the torque-measurements for the more concentrated specimens owing to instability of the inner cylinder. A small difference in the height of the column of liquid, made with the object of detecting an end effect, did not alter the velocity-gradients but affected the torque-measurements in the proportion of the wetted surface. Results, the suspensions of four different concentrations, are shown in figures 5, 6, 7, 8. They all, with the exception of the weakest, exhibit gradients varying notably in the neighbourhood of the inner cylinder.

§ 3. THEORY

Theories of colloid viscosity may be grouped under two types:

(i) The hypothesis of structural friction. Buckingham* supposed that, in addition to a viscous force proportional to the velocity-gradient dv/dy between neighbouring annuli, there was a constant force a due to friction between the disperse phase and the neighbouring liquid. Newton's law then becomes v, y a

$$F = (a - \eta\, dv/dy)\, dS \qquad \text{......(1)},$$

η being the coefficient of viscosity and dS an element of area. This theory predicts an outer section of fluid endowed with a constant angular velocity in the case of the concentric-cylinder apparatus, moving *en bloc* with the outer cylinder. This theory Pichot† thinks to be confirmed by his measurements with gelatine in a flow tube. The theory also predicts a limiting shear, below which no flow should take place. This limiting stress has unfortunately never been observed. η, dS

(ii) The hypothesis that the viscosity-coefficient is variable and a function of the velocity-gradient. Porter and Rao‡ write

$$\eta = \eta_0\, (dv/dy)^{-n}. \qquad n$$

For the heterogeneous liquids, for which n is given a small positive value while it is zero for the homogeneous liquids, velocity-gradients similar to those given by the first theory can be constructed. This theory has the advantage that no static friction is expected of the fluid. Newton's law, on this theory, becomes

$$-F = \eta_0\, (dv/dy)^{1-n}\, dS \qquad \text{......(2)}.$$

In the case of the concentric cylinder, the velocity-gradient at any radial distance r being $r d\omega/dr$, the moment of the annulus about the axis is $2\pi r\eta\, (r\, d\omega/dr)\, r$ per unit length, and this moment is the same for every value of r in steady motion, so that the torque τ is proportional to $r^3\eta\, d\omega/dr$. Thus $\tau\, (r^3 d\omega/dr)^{-1}$ should be a measure of relative viscosity. Accordingly, for each of the suspensions of figures 6, 7, 8, the slope of the *angular-velocity* curves was first plotted against r, and hence $\tau\, (r^3\, d\omega/dr)^{-1}$ could be plotted against $r\, d\omega/dr$, the appropriate torque being read from figure 4. The resulting (viscosity, velocity-gradient) curves are shown on r, ω τ

---

* *Proc. Amer. Soc. Tent Materials*, **21**, 1154 (1921).

† *J. de Physique*, **3**, 205 (1932).

‡ *Trans. Farad. Soc.* **23**, 311 (1927).

figure 9, the pure solvent being included, for purposes of comparison, at its absolute value ($\eta = 0{\cdot}012$).

Each suspension shows a diminishing viscosity as the velocity-gradient increases, tending however to an asymptotic value at high velocity-gradients. The flow is in fact nearly normal at high velocity-gradients, unless turbulence intervenes. A noteworthy example of this normal flow occurs in the top curve of figure 6. By plotting log η against log $(r\,d\omega/dr)$ the mean values of n were found to be 0·55 and 0·75 respectively for the two medium suspensions, and 0·9 for the paste. These values are of the same order as those deduced by Farrow, Lowe and Neale* by semi-empirical methods from outflow measurements in capillary tubes. An exponential formula such as that suggested by Reiner and Riwlin† might also be fitted to the curves. Finally,

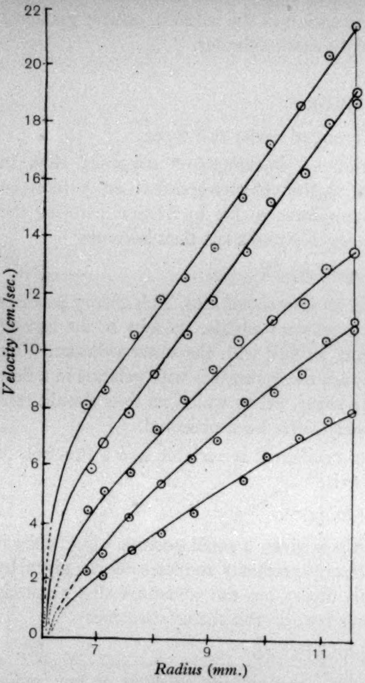


Figure 7. Velocity-gradients in 31·2-per-cent suspension.

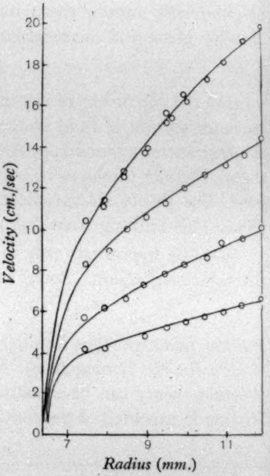


Figure 8. Velocity-gradients in 54·5-per-cent suspension.

---

* *J. Test Institute*, **19**, T 18 (1928).

† *Kolloid. Z.* **43**, 72 (1927); **44**, 9 (1928).

in figure 10 we have plotted η against concentration by volume for several values of velocity-gradient, including data for an 18-per-cent suspension for which the curves are not reproduced. The deduction of Einstein* from Stokes's law, that the viscosity should be a linear function of the concentration, fails at large concentrations, but at high velocity-gradients the variation of η with concentration approximates to that of an ideal suspension, conforming to Newton's and Einstein's laws.

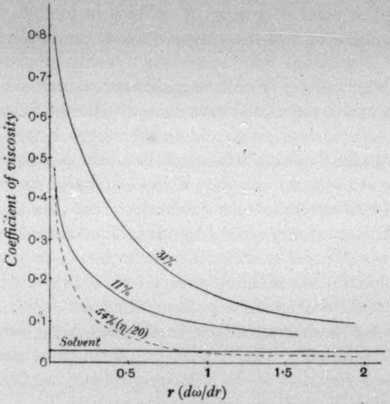


Figure 9. Variation of viscosity with velocity-gradient.

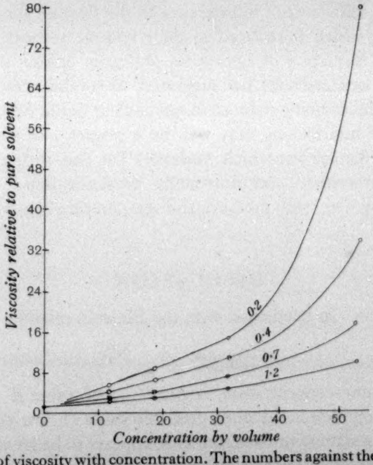


Figure 10. Variation of viscosity with concentration. The numbers against the curves denote $r(d\omega/dr)$.

---

* *Ann. der Phys.* **19**, 289 (1906); cf. Humphrey and Hatschek, *loc. cit.*

§4. CONCLUSIONS

These results, which we believe to be the first systematic measurement of velocity from point to point in a series of colloids in motion, confirm the earlier deductions from integrated flow-measurements that the coefficient of viscosity in a disperse system diminishes with increasing velocity-gradient, but tends to a constant value at high rates of shear. At moderate rates of shear the distribution of flow in the concentric-cylinder system is such that the velocity falls gradually from the outer cylinder inwards, with a more rapid drop at the surface of the inner cylinder. We have indeed assumed the condition of no slip at the solid boundary. That there is none at the outer cylinder, at least, is shown by the velocity graphs, and our extrapolation to zero velocity at the surface of the inner cylinder is confirmed by the torque on the latter, for in each of figures 6, 7 and 8, the ratio torque/velocity-gradient at the inner cylinder is a constant for a particular suspension, although the ratio torque/velocity of the outer cylinder is not. Neither is there sure evidence of a yield value, such as the Buckingham theory requires*. The smallest shear which we applied started the fluid into motion. In this theory the force a, equation (1), which many writers identify with a solid-liquid friction, need not indeed be constant; it can be a function of the velocity-gradient, vanishing with the flow. With this modification, indeed, the two theories coalesce.

As to the ultimate cause of anomalous viscosity, these experiments tell little, except that there is some sort of interference to the flow on the part of particles of the disperse phase, which is reduced as their relative velocity is increased. This may be due to the formation of aggregates gradually broken down as the rate of shear increases, or, as Hatschek† has suggested, to combination of the two phases, the particles so produced being reduced in size as their liquid envelopes are shorn off. That some form of interlocking may well be a property of even a homogeneous liquid is shown by the success which Andrade‡ has had with a formula, based on his concept of "transitory and fluctuating crystallization," which covers the variation of viscosity with both pressure and temperature in a homogeneous liquid.

DISCUSSION

Mr E. W. MADGE. In connexion with the Einstein relation

$$\eta/\eta_{\substack{\text{dispersion}\\\text{medium}}} = 1 + K\theta,$$

where θ is the volume concentration, it would be of value if the authors would state what in their opinion is the most probable value of K over the linear portion of the curve. Such a statement based on what appears to be an accurable method of investigating the flow of suspensions would no doubt serve to settle the differences of opinion concerning the hypotheses on the basis of which such a formula is derived.

---

* Except in the case of the thick paste.

† *Kolloid. Z.* **40**, 53 (1926).

‡ *Nature*, **125**, 309, 580 (1930).

The linear formula also implies that the viscosity relative to the dispersion medium depends only on the total volume of the suspended particles and not on their actual dimensions. It would be interesting to know whether the authors have in mind extending their work to determine over what range this is valid.

AUTHORS' reply. Owing to the dependence of η on velocity-gradient even at low concentrations, it is rather difficult to deduce a precise value for K from the experiments. If we understand Einstein's formula correctly, it depends on the laws of classical hydrodynamics and assumes no material interference between the suspended particles or adsorption of the dispersion medium. The existence of anomalous viscosity seems to indicate that such interference does in fact take place. If this be so, the application of Einstein's formula to suspensions seems of doubtful validity, but we agree that an investigation of the effect of the size of the particles would be useful. However, on the assumption that the interference is least when the rate of shear is large, the flow then approaching most closely that of a homogeneous fluid, the value of K in the experiments was of the order of that (2·5) deduced theoretically by Einstein.

551.594.12:551.51.051

THE INFLUENCE OF ATMOSPHERIC SUSPENSOIDS UPON THE EARTH'S ELECTRIC FIELD AS INDICATED BY OBSERVATIONS AT KEW OBSERVATORY

By H. L. WRIGHT, M.A.

Communicated by Dr F. J. W. Whipple, October 7, 1932. Read December 2, 1932.

ABSTRACT. Changes in the electrical resistivity of the air and in the potential-gradient may be associated with changes in the concentration of gross particles and of condensation nuclei. Observations of these four quantities made at Kew Observatory over a period of three years are analysed with a view to formulating functional relations between them. The observations indicate that resistivity depends upon the number of gross particles and of condensation nuclei, while potential-gradient varies with resistivity and the number of nuclei. The theoretical implications of this statement are considered.

§ 1. INTRODUCTION

Our knowledge of the electrical conditions of the atmosphere is derived very largely from observations of the potential-gradient near the earth's surface. Continuous records of potential-gradient have been accumulated for many years now at numerous stations widely distributed in geographical position. Observations are thus plentiful, and the changes in potential-gradient have been extensively studied, but why these changes occur is not yet completely understood.

At any one station the potential-gradient is subject to certain variations which are regular and well defined, and especially is this the case with the diurnal variation. But when the diurnal variations at different stations are compared, it is found that they do not all conform to one particular type, either in amplitude or in phase angle. Sometimes a difference even of period is found, the potential-gradient at certain stations having two maxima and minima each day, that at others having only one maximum and minimum.

Some degree of uniformity was introduced when Mauchly found⁽¹⁾ that the diurnal variation of potential-gradient over the oceans proceeds according to universal time and not local time. Shortly before this Hoffmann, comparing observations in polar regions, noticed⁽²⁾ that the principal maxima and minima in the diurnal variation agreed if the hours were referred to universal time. Mauchly later analysed⁽³⁾ the readings at observatories in different parts of the world and found indications of a diurnal oscillation in universal time. Whipple has shown⁽⁴⁾ that this oscillation is similar to the diurnal frequency of thunderstorms all over the world.

Much earlier, Chree and Watson had pointed out⁽⁵⁾ that the diurnal variation of potential-gradient at Kew Observatory is remarkably similar to that of atmospheric pollution. Now atmospheric pollution is evidently a local phenomenon, and therefore it follows that potential-gradient is a function of local time, at any rate in polluted areas. More recently Whipple has shown(6) that the adoption of summer time in Great Britain, whereby the clock is put forward one hour in summer, has resulted in a displacement of the morning maximum and minimum of potential-gradient in summer, the G.m.t. of their occurrence now being one hour earlier than before the introduction of summer time. Thus the maximum and minimum in summer occur at the same hours as before by the civil clock, but are one hour earlier by the sun and by Greenwich time. More definite evidence that the diurnal variation of potential-gradient is affected by local phenomena could scarcely be expected.

The conclusion is irresistible that the diurnal variation of potential-gradient is governed by two factors, one of which is a function of universal time, the other of local time. At certain stations the universal term may predominate, at others the local term, and the magnitude of the local term obviously depends upon local conditions. For future interpretation of the diurnal variation of potential-gradient it becomes increasingly important to know what proportion of the local variation is due to the local term, and this presupposes a full knowledge of the dependence of the local term on local conditions. The purpose of the present paper is to investigate the effect upon the local electric field of the two types of atmospheric suspensoids: condensation nuclei, and the larger, opaque particles which at Kew Observatory are mainly particles of smoke.

The work of Chree and Watson shows the effect of the gross particles alone, though the unit employed by them was not the individual particle but the total weight of suspended matter. Special interest is attached to the correlation of the number of particles with electrical conditions, because the reaction is likely to depend upon the individual particles rather than on their total weight. Wait(7) and Builder(8) have investigated the effect of nuclei separately on potential-gradient and the electrical conductivity of the air. No work is known to the writer in which the effect of gross particles and condensation nuclei conjointly has been considered.

§ 2. OBSERVATIONS AT KEW OBSERVATORY*

At Kew Observatory observations of the electrical conductivity of the air have been made regularly for many years at 15 h. G.m.t. on fine days. Since the beginning of 1928 observations of the concentrations of gross particles and condensation nuclei have been made at the same time, as opportunity offers.

The observation of conductivity is made with a Wilson gold-leaf electrometer set on a tripod. Details of the method of observing are given in a memoir by Watson(9) in which reasons are adduced for believing that the element which is measured is the positive unipolar conductivity. The presence of the tripod results in a disturbance of the equipotential surfaces, the potential-gradient over the test plate of the electrometer being increased about six-fold. In winter, when the gradient is high, the congestion of the equipotential surfaces may produce a "saturation" effect the consequence of which is to give a value for the conductivity which is artificially low.

---

* Certain modifications of the routine observations have been made since the period dealt with in this paper.

The observation of conductivity takes half an hour, and between the times at which the gold leaf is read observations of the concentration of condensation nuclei are made with an Aitken nucleus counter (10). As nearly as possible at 15 h. a sample of air is introduced into an Owens jet dust counter (11) and the gross particles contained in this sample are subsequently counted* under a microscope. The observations of condensation nuclei and gross particles for the three years 1928–30 which are utilized in the present work are discussed in a paper by the writer (12).

The potential-gradient is recorded continuously at Kew Observatory by a Kelvin water-dropper. Particulars of the methods used to standardize the water-dropper are to be found in the Observatories Year Book (13). The values of the potential-gradient and conductivity which form the subject of the present investigation are published in the same work.

It should be noted that the values of conductivity are the means for a period of about half an hour centred at 15 h., those of potential-gradient are the means for an hour centred at 15 h. The values of the concentration of condensation nuclei are the means for about twenty minutes centred at 15 h., while the values of the concentration of gross particles are instantaneous values. All the observations under discussion were made out of doors and in dry weather only.

In view of the reciprocal relation which is found to exist between the conductivity and each of the quantities (1) concentration of gross particles, (2) concentration of nuclei, (3) potential-gradient, it is more convenient to utilize the reciprocal of conductivity, which is here termed *resistivity*. The effect of saturation in winter is to give enhanced values of resistivity. It should therefore be borne in mind that when resistivity is high the true value is probably less than that which is given here.

Monthly means of the four elements under review are given in table 1. Since 15 h. is approximately the time of day at which a minimum of all four quantities is to be expected, the true monthly averages are considerably higher than those given in the table. A graphical representation of the results contained in table 1 is shown in figure 1. The resemblance of the behaviour of all four quantities is striking.

The annual inequalities may be resolved by harmonic analysis; the value of the element being

$$c_0 + c_1 \sin (t + \alpha_1) + c_2 \sin (2t + \alpha_2) + \dots,$$

where the unit of time is such that 1 year $= 2\pi$, the values of the amplitudes c_1 and phase angles α_1 of the first harmonic term are as given at the foot of table 1. The agreement in phase angle is noteworthy, the minimum of all four quantities occurring in the middle of July within a few days of each other. But no great significance can be attached to this coincidence, for most meteorological elements subject to a well-defined annual variation have turning points at about this time of year.

---

* According to an investigation carried out by Prof. Whytlaw-Gray, on behalf of the Atmospheric Pollution Research Committee of the Department of Scientific and Industrial Research, the number of particles given by the Owens instrument is about a fifth of the number present in the air and large enough to be seen by a microscope. The details of this investigation have not yet been published.

The association between these four quantities will now be examined in greater detail. The influence of particles and nuclei on resistivity will be dealt with first, and their effect on potential-gradient will be considered later.

Table 1. Monthly averages, Kew Observatory, 1928–30, 15 h. G.m.t. Dry weather.

Month	Gross particles (No. per cm³)	Condensation nuclei (No. per cm³)	Resistivity (10^{16} Ω.-cm.)	Potential-gradient (V./cm.)
January	1670	43,000	10·8	4·27
February	1560	35,000	11·2	4·61
March	880	31,000	6·9	3·42
April	414	23,000	3·2	2·75
May	231	26,000	3·1	2·21
June	60	15,000	2·4	1·81
July	60	21,000	2·0	1·54
August	86	15,000	1·9	1·67
September	226	19,000	2·5	2·26
October	345	27,000	3·8	2·76
November	1245	36,000	8·6	3·48
December	2400	55,000	11·8	4·50
Mean: c_0	765	29,000	5·7	2·94
Amplitude: c_1	964	14,300	5·0	1·49
Phase angle: α_1	82°	83°	78°	73°

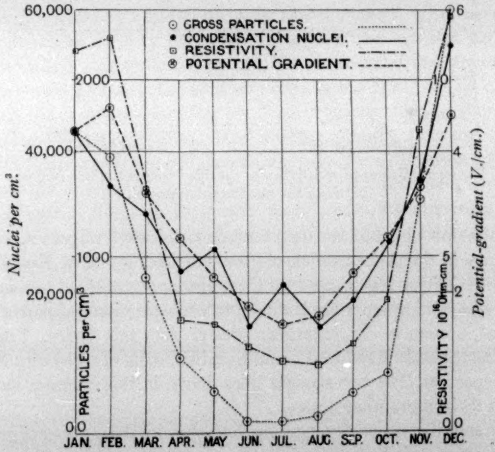


Figure 1. Annual variation, 1928–30, Kew Observatory, 15 h. G.m.t.

§3. SUSPENSOIDS AND RESISTIVITY

Individual observations have been grouped according to the concentration, firstly, of gross particles, and secondly, of condensation nuclei. For each such group the mean of the associated values of resistivity was determined. Since each group covers for the most part only a small range of numbers of particles or numbers of nuclei, as the case may be, the middle number of each group may be taken to represent with sufficient accuracy the average of the numbers of particles or of nuclei in the group. Thus we may associate the mean value of resistivity for each group with the middle number of particles or nuclei of that group.

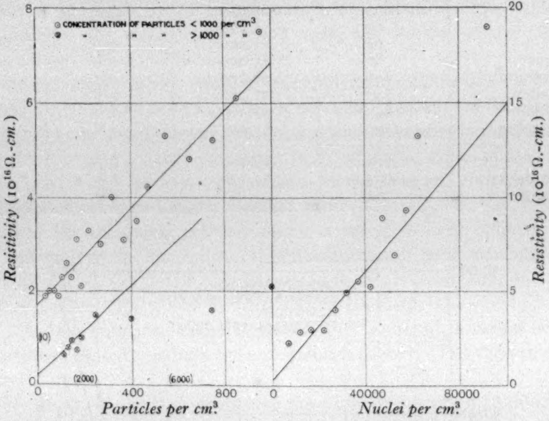


Figure 2. Values of resistivity for specified concentrations of gross particles and condensation nuclei.

The results thus obtained are represented graphically in figure 2. Owing to the extensive range in the concentration of gross particles found at Kew Observatory, the values of resistivity associated with these are represented on two scales. In the left-hand diagram of figure 2 circles refer to concentrations of particles less than 1000 per cm³, crosses to concentrations greater than this figure. For the higher concentrations the scale is reduced tenfold, and the scale of resistivity is reduced in the same proportion. The two straight lines drawn in this diagram have the same equation, on their appropriate scales.

It may be seen that resistivity increases linearly with the number of gross particles until concentrations of the order of 3000 per cm³ are reached. Beyond this point the resistivity increases more slowly with increasing pollution. The following argument shows that this is to be expected. The conductivity is composed of two parts, that due to small ions and that due to large ions. Ordinarily the contribution from large ions is so small as to be negligible, but increasing pollution is associated with enhanced concentrations of large ions, and the contribution of these to the conductivity then becomes appreciable. By so much is the resistivity reduced.

It may be mentioned that a concentration of gross particles greater than 3000 per cm.^{3} at 15 h. is normally associated with conditions of mist or fog.

That the straight lines drawn through the points in the diagram do not pass through the origin is also to be expected, for if gross particles were completely absent the resistivity would not be zero.

The association between resistivity and the number of nuclei is shown in the right-hand diagram of figure 2. A straight line may be drawn to pass through the points with fair accuracy, though a curve may at first sight seem to give a better representation of their distribution. It is to be remembered, however, that high values of resistivity are probably enhanced artificially, and the departure from linearity indicated by these may not necessarily be valid. At the other end of the scale, where a departure from linearity appears to be suggested, there are theoretical reasons for believing that the curve should pass near the origin: the resistivity of air free from nuclei would depend only on the recombination of small ions, and the resistivity would then be such that on the scale used in the diagram it would appear to be very close to the origin*. All things considered, there seems to be no cogent reason at this stage for departing from a linear relationship.

That resistivity increases more rapidly with enhanced concentrations of nuclei is not in accordance with the argument put forward above, which applies equally to the case of nuclei, whereby a falling off in the rate of increase of resistivity with enhanced concentrations is to be expected. In spite of the fact that high values of resistivity are unduly augmented, we might have anticipated that the points representing these would lie below the optimum line, as was found in the case of gross particles. That the points representing low concentrations of nuclei should lie above this straight line is also unexplained. It is, however, almost certain that the points in the diagram in figure 2 may not be taken to represent purely the association between resistivity and the number of nuclei; for, if part of the resistivity is due to gross particles, that part is likely to be greater when nuclei are numerous than when nuclei are few, owing to the number of gross particles being greater when nuclei are more numerous.

It is necessary therefore to consider simultaneous values of all three quantities. The observations may be grouped according to values of resistivity, and mean values

---

* For air free from nuclei the resistivity

$$R = \frac{1}{ek}\sqrt{\left(\frac{\alpha}{q}\right)}\ \Omega.\text{-cm.},$$

where e is the electronic charge per ion, $15{\cdot}9 \times 10^{-20}$ coulombs;
k the mobility of small ions, $1{\cdot}3$ cm./sec. per V./cm.;
α the recombination coefficient of small ions, $1{\cdot}6 \times 10^{-6}$; and
q the rate of production of ions per cm.^{3} per sec.

If q is between 10 and 20, values appropriate to land stations, R is between $0{\cdot}1 \times 10^{16}$ and $0{\cdot}2 \times 10^{16}$ Ω.-cm.

of particles and nuclei determined for each group. The results obtained by grouping in this way are shown in table 2.

Table 2. Average concentrations.

The number of observations in each group is shown by the figures in brackets.

Resistivity (10^{16} Ω.-cm.)	Gross particles (No./cm.^{3})	Condensation nuclei (No./cm.^{3})	Resistivity (10^{16} Ω.-cm.)	Gross particles (No./cm.^{3})	Condensation nuclei (No./cm.^{3})
1·0–1·4 (12)	105	13,800	5·0–5·9 (11)	582	30,100
1·5–1·9 (11)	123	23,600	6, 7 (11)	1380	33,000
2·0–2·4 (10)	148	23,200	8, 9 (10)	1250	40,000
2·5–2·9 (16)	217	25,600	10, 11 (7)	2050	38,000
3·0–3·4 (12)	293	27,000	12, 13 (5)	4470	54,000
3·5–3·9 (9)	321	22,200	14, 17 (11)	5240	69,000
4·0–4·9 (10)	676	30,700	20–25 (4)	8050	71,000

A graphical representation may be made by selecting one of the variables as divisor and plotting the two resulting quotients against one another. Accordingly the middle value of resistivity for each group and the associated number of nuclei have been divided by the associated value of the number of particles, and the quotients are plotted in figure 3. Against each point in the diagram is placed the value of resistivity in units of 10^{16} Ω.-cm.

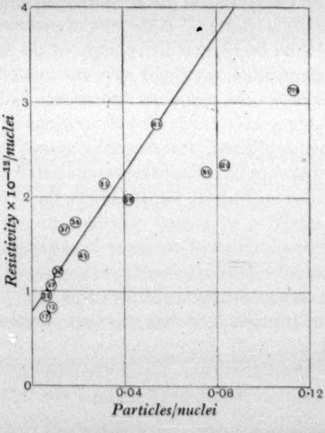


Figure 3. Illustrating the results contained in table 2.

Owing to the limitations of the observations of resistivity, no great significance can be attached to the points representing values of resistivity above 12×10^{16} Ω.-cm. It may be seen that the remainder lie fairly closely to a straight line.

The position of this straight line illustrates very clearly that the effect of gross particles on resistivity is not negligible. If the resistivity depended only on the number of nuclei we should expect the optimum line to be parallel with the horizontal axis. This is far from being the case.

The equation of the straight line to which figure 3 has been drawn is

$$10^{-12} R = 37P + 0{\cdot}77N \qquad \text{......(1)},$$

where P and N denote the concentrations of particles and nuclei respectively per cm.³ ***P, N***

§4. CORRELATION OF INDIVIDUAL OBSERVATIONS

So far we have been considering group means, and have found from these that resistivity appears to depend on both particles and nuclei more or less in accordance with a law represented by equation (1). It is necessary, however, to show that these results are borne out by the individual observations.

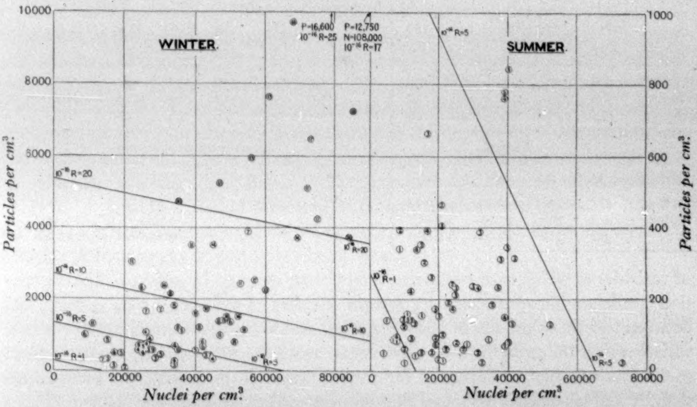


Figure 4. Simultaneous values of resistivity (10^{16} Ω.-cm.), and numbers of particles and nuclei per cm.³

In figure 4 are represented the simultaneous concentrations of particles and nuclei at the time of resistivity observations. The associated value of resistivity, in units of 10^{16} Ω.-cm., is placed over the representative point. Owing to the extensive range in the number of gross particles the observations in winter and summer are represented in two separate diagrams; while the scale of nucleation is the same in each diagram, the scale of concentration of particles is ten times larger in the summer diagram than in the winter diagram. If a definite value of nucleation is selected, e.g. 30,000, it may be seen that while in summer only low values of resistivity are found on this ordinate, in winter considerably higher values are found on the same ordinate. This shows very clearly the effect on resistivity of the presence of gross particles. Isopleths of resistivity have been drawn in the figure from equation (1). On the whole this equation fits the observations quite well.

A more detailed analysis may be made by a statistical correlation of the individual observations by the method of least squares. For this purpose all the available observations extending over the three years have been utilized, the number of simultaneous observations of resistivity and gross particles being 251, and the number of simultaneous observations of resistivity and nuclei being 240. It is desirable to treat separately the two seasons of summer (April to September) and winter (October to March) owing to the uncertainty of the high values of resistivity in winter.

The correlation coefficients are given in columns (1) and (2) of table 3, the pair of variables to which each coefficient refers being denoted by suffixes. The correlation coefficient between resistivity and the number of particles is 0·74 ± 0·03; that between resistivity and the number of nuclei is 0·73 ± 0·03. Corrections for annual variation may be made to these coefficients, using the harmonic expressions given at the foot of table 1. Corrected for annual variation, the coefficient between resistivity and particles is 0·73, and that between resistivity and nuclei is 0·70. These are practically the same as the uncorrected coefficients; thus the strong correlations are not due to similarity in the annual variation of the three variables.

Table 3. Correlation coefficients.

	Resistivity					Potential-gradient							
	Total			Partial		Total			Partial				
	(1) r_{RP}	(2) r_{RN}	(3) r_{NP}	(4) $r_{RP.N}$	(5) $r_{RN.P}$	(6) r_{XR}	(7) r_{XP}	(8) r_{XN}	(9) $r_{XP.N}$	(10) $r_{XN.P}$	(11) $r_{XR.NP}$	(12) $r_{XP.RN}$	(13) $r_{XN.RP}$
Summer	·66	·42	·25	·63	·36	·72	·54	·39	·49	·31	·53	·12	·13
Winter	·66	·74	·71	·29	·52	·56	·51	·63	·12	·45	·14	·07	·34
Year	·74	·73	·69	·48	·46	·72	·60	·65	·28	·41	·40	·07	·32
	Means					Standard deviations							
	X	R	P	N		X		R		P		N	
Summer	2·1	2·5	220	23,000		1·1		1·3		230		13,000	
Winter	4·3	8·5	2100	40,000		1·7		5·8		2500		19,000	
Year	3·2	5·2	1300	31,000		1·8		5·0		2000		18,000	

A high correlation between resistivity and nuclei is to be expected: it is well known that the number of nuclei largely governs the number of small ions and hence the resistivity. That gross particles are also effective has not up to the present been well established, and the novelty of this feature renders it liable to suspicion. It may at first be thought that the strong correlation found between resistivity and the number of particles is due to the association between particles and nuclei; for both particles and nuclei are produced by combustion, and meteorological conditions which favour the accumulation of the one also favour the accumulation of the other. Hence there is a tendency for particles and nuclei to increase and decrease together. The correlation coefficients between these two from 169 observations are given in the third column of table 3. It may be seen that in winter the correlation between the numbers of particles and nuclei is strong; in summer it is weaker but still positive.

It is necessary, therefore, to obtain a measure of the correlation between resistivity and the number of gross particles when the association of each with nuclei has been eliminated. This may be done by the method of partial correlation whereby the separate effects of each variable may be isolated. Partial correlation coefficients* are given in columns (4) and (5) of table 3, the notation being used in which the suffixes to the left of the point denote the two variables correlated and the suffix to the right denotes the variable the effect of which has been eliminated. It will be seen that in summer the partial coefficient between resistivity and the number of gross particles is greater than that between resistivity and the number of nuclei; in winter it is less. On the average, for the year as a whole, the partial coefficients are about the same. It follows that the high correlation between the number of particles and resistivity is not due to mutual associations with nuclei, and that gross particles can be at least as effective as nuclei in determining the resistivity.

Values of the means and standard deviations are included in table 3. The mean and standard deviation of R from simultaneous observations of R and P are not quite the same as the mean and standard deviation of R from simultaneous observations of R and N. Later it becomes necessary to correlate R with the potential-gradient, and the mean and standard deviation of R from this set of observations are also slightly different. These differences are however small, and the values given in the table are the means of all three. The same remark applies to the other variables.

If the regression equation is formed from the partial correlation coefficients and the values of the means and standard deviations are substituted, the equation expressing R in terms of P and N is found to be

$$10^{-16}R = 11 \times 10^{-4}P + 1\cdot2 \times 10^{-4}N + 0\cdot2 \pm 3\cdot0\,Ca \qquad \ldots\ldots(2),$$

where Ca denotes a casual number† the standard value of which is unity. If the casual term is ignored, the correlation coefficient between the two sides of this equation is 0·80. *Ca*

The coefficients in equation (2) are not the same as those given in equation (1). This is because high values of R are included in (2), whereas in (1) these were deliberately ignored. In view of the influence of the high values of R, of which the validity is doubtful, on the coefficients in (2), and of the good fit of equation (1) to the individual observations as shown in figure 4, it seems likely that the coefficients in (1) may be more reliable than those in (2). The accuracy of the coefficients in either of these equations may not however be insisted upon.

It is to be noted that the residual term 0·2 in equation (2) is much less than the standard value of the casual term. A large residual term would mean that the

---

* The coefficients are determined by such formulae as

$$r_{12\cdot3} = (r_{12} - r_{13}r_{23})(1 - r_{13}^2)^{-\frac{1}{2}}(1 - r_{23}^2)^{-\frac{1}{2}}.$$

† This notation is due to Whipple⁽¹⁴⁾. In this particular example, 3·0 is the standard error of a determination of $10^{-16}R$ from the terms in P and N.

resistivity depended on other influences besides nuclei and particles. That the residual term is inappreciable suggests that the local resistivity may be wholly accounted for by the concentrations of nuclei and gross particles.

§5. RESISTIVITY AND POTENTIAL-GRADIENT

Before going on to examine the variations in potential-gradient with different concentrations of atmospheric suspensoids, it is desirable first to trace the association between potential-gradient and resistivity. The values of potential-gradient on occasions when the resistivity was within specified limits have been grouped together, and the mean for each group has been derived. These means are given in table 4, and the results are represented graphically in figure 5.

Table 4.

The number of observations in each group is shown by the figures in brackets.

Resistivity (10^{16} Ω.-cm.)	Potential-gradient (V./cm.)	Resistivity (10^{16} Ω.-cm.)	Potential-gradient (V./cm.)
0·9–1·1	1·56 (8)	4·1–4·5	3·46 (13)
1·2–1·4	1·50 (39)	4·6–5·5	3·55 (24)
1·5–1·7	1·59 (21)	5·6–6·5	3·93 (18)
1·8–2·0	1·83 (35)	6·6–7·5	4·87 (17)
2·1–2·3	1·86 (32)	7·6–8·5	4·72 (16)
2·4–2·6	2·12 (23)	9, 10	5·12 (12)
2·7–2·9	2·18 (25)	11–13	5·41 (14)
3·0–3·2	2·47 (14)	14–17	5·94 (17)
3·3–3·5	2·65 (18)	20–33	5·55 (11)
3·6–4·0	2·85 (29)	—	—

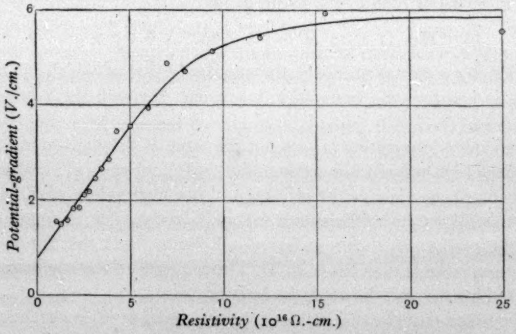


Figure 5. Values of potential-gradient for specified resistivity.

The points in the graph do not lie along a straight line through the origin as might have been expected from Ohm's law if the air-earth current at Kew had been constant. A straight line may be drawn through the origin so as to pass close to the points representing values of resistivity less than about 4 × 10^{16} Ω.-cm., but the falling off for values of resistivity above this figure is very evident. The points representing high values of resistivity are undoubtedly less reliable, but the curvature is apparent for much lower values than can be disregarded.

A correlation of the individual observations has been made, all the available observations extending over the three years, 390 in number, being utilized. The correlation coefficients thus obtained are given in column (6) of table 3. From all the observations the correlation coefficient between potential-gradient and resistivity is $0{\cdot}72 \pm 0{\cdot}04$; corrected for annual variation by use of the harmonic expressions in table 1 the value is 0·57. The correlation is stronger in summer than in winter; thus changes in potential-gradient and resistivity are more closely related in summer than in winter. It is possible that the error attached to the high values of resistivity in winter reduces the coefficient for this season.

The coefficients are on the whole lower than might have been expected. They are of course worked out on the basis of linear regression. The graph in figure 5 suggests that the relation between resistivity and potential-gradient may not be linear. In order to allow for a departure from linearity, additional coefficients have been worked out, as a matter of interest, on the basis of a logarithmic regression; that is, potential-gradient was correlated with the logarithm of resistivity. The values of the coefficients were found to be 0·60 for summer, 0·65 for winter, and 0·79 for the year. Thus very little improvement in the value for the year is obtained by departing from a linear regression, and the value for summer becomes definitely reduced. The weakness in the correlation based on linear regression appears therefore to be due less to the non-linearity of the resistivity potential-gradient curve than to the occurrence of changes in potential-gradient in addition to those consequent upon changes in resistivity.

§6. SUSPENSOIDS AND POTENTIAL-GRADIENT

Simultaneous observations of suspensoids and potential-gradient may be analyzed by methods similar to those used to trace the association between suspensoids and resistivity. Accordingly the observations have been grouped according to the concentrations firstly of particles and secondly of nuclei, and mean values of potential-gradient have been derived for each group. The results thus obtained are illustrated in figure 6, two scales again being used in the case of gross particles owing to the difficulty of representing the extensive range of these on a single scale.

It may be seen from the diagram that potential-gradient increases with increasing concentration of particles, rapidly at first but more slowly later. The points do not appear to follow a straight line, the form of the graph resembling to some extent that between potential-gradient and resistivity. This suggests that gross particles affect potential-gradient only in so far as they lead to changes in resistivity. It will be seen later that this suggestion is supported by other considerations.

The points representing the association between potential-gradient and condensation nuclei are distributed closely about a straight line. It may be noted that this straight line does not pass through the origin.

If we consider simultaneous values of all three elements and group the observations according to the value of the potential-gradient, we may determine the mean numbers of particles and nuclei associated with values of potential-gradient within specified limits. The results obtained by grouping in this way are shown in table 5. The last group in the table includes values of potential-gradient varying from 6·60 to 8·90 V./cm., the mean value for the group being 7·55 V./cm.

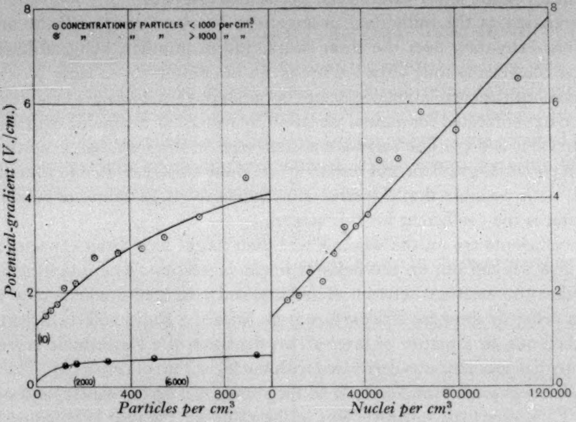


Figure 6. Values of potential-gradient for specified concentrations of gross particles and condensation nuclei.

Table 5. Simultaneous concentrations.

The number of observations in each group is shown by the figures in brackets.

Potential-gradient (V./cm.)	Smoke particles (No./cm³)	Condensation nuclei (No./cm³)	Potential-gradient (V./cm.)	Smoke particles (No./cm³)	Condensation nuclei (No./cm³)
0·75–1·45 (20)	209	23,500	4·00–4·45 (6)	2310	45,500
1·50–1·95 (27)	271	20,000	4·50–4·95 (5)	1470	34,000
2·00–2·45 (24)	349	23,000	5·00–5·45 (10)	2100	44,000
2·50–2·95 (17)	877	29,500	5·50–5·95 (8)	2740	56,500
3·00–3·45 (13)	744	30,500	6·00–6·45 (5)	1700	42,000
3·50–3·95 (13)	568	31,000	> 6·50 (11)	4650	63,000

The results given in table 5 may be illustrated graphically by selecting one variable as a divisor and plotting the two resulting quotients. If the number of gross particles is selected as divisor the graph between the two resulting quotients is as shown in figure 7. Against each point in the diagram is placed the associated value of the potential-gradient. With but one exception the points are clustered fairly uniformly about a straight line. This straight line passes very close to, if not through, the origin. If it does indeed pass through the origin the equation of the functional relation between X/P and N/P is reduced to the form

$$X = aN,$$

where X is the potential-gradient and N is the concentration of nuclei. This means that X is independent of P, the number of gross particles.

X, N
P

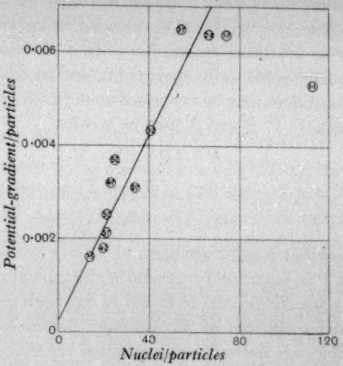


Figure 7. Illustrating the results contained in table 5.

§7. CORRELATION OF INDIVIDUAL OBSERVATIONS

A statistical analysis of the individual observations serves to show the strength of the association between suspensoids and potential-gradient, and gives some information as to why the association exists. Correlation coefficients between potential-gradient and the number of particles and nuclei are given in columns (7) and (8) of table 3, the two seasons of winter and summer being treated separately as in the case of resistivity. It may be mentioned that in working out the coefficients a few occasions of negative potential-gradient were rejected at the outset, but all the available positive values of potential-gradient have been utilized, the number of simultaneous observations of potential-gradient and gross particles being 286, and the number of simultaneous observations of potential-gradient and nuclei being 275.

The correlation coefficient between potential-gradient and the number of gross particles is 0·60 ± 0·04; corrected for annual variation by means of the harmonic expressions in table 1, the coefficient is 0·53. The coefficient between potential-gradient and the number of nuclei is 0·65 ± 0·03, and when corrected for annual variation 0·47. Neither coefficient is particularly high, though both are too significant to be neglected.

By combining these coefficients with those in column (3) between particles and nuclei, we may evaluate partial coefficients, representing the degree of association between potential-gradient and suspensoids when the mutual association between the two types of suspensoids is eliminated. The partial coefficients thus obtained are shown in columns (9) and (10) of table 3. The partial coefficient between potential-gradient and the number of particles is only 0·28 and is practically negligible in winter, confirming the suggestion of figure 7 that the association between potential-gradient and the number of gross particles is but slight. The partial coefficient between potential-gradient and the number of nuclei is 0·41, a figure of some but not considerable significance.

The following question now arises. Is the association between potential-gradient and suspensoids due to a mutual association with resistivity, or does potential-gradient depend on suspensoids quite apart from, and in addition to, its variation with resistivity? This question may be expressed analytically as follows. The general linear equation between X, P, R and N may be written

a, b, c, d

$$X = aR + bP + cN + d \qquad \ldots\ldots(3).$$

If b and c are zero, X is still a function of P and N in consequence of the relation

e, f

$$R = eP + fN,$$

and the question is whether b and c are zero.

The coefficient of P in equation (3) is zero if the partial correlation coefficient of X with P when the association due to R and N has been eliminated is zero; and the same is true of the coefficient of N. Although partial coefficients connecting more than three variables are not ordinarily of much value, it seems worth while in this case to obtain the partial correlation coefficients between X and each one of R, P and N, when the effect of the other two has been eliminated. The coefficients thus obtained are as given in columns (11) to (13) of table 3.

It may be seen that the partial correlation coefficient between potential-gradient and the concentration of gross particles is so small as to be negligible, and this is true both in winter and in summer. Thus there is justification for stating that gross particles affect potential-gradient only in so far as they lead to changes in resistivity. The largest of the coefficients is that between potential-gradient and resistivity. This is however small in winter. As has been pointed out, the weakness of the correlation in winter may be due to errors in high values of resistivity. Condensation nuclei appear to have a small residual influence on potential-gradient in addition to their effect through resistivity, but this residual influence is practically negligible in summer. Consideration of the seasonal values of the coefficients suggests that changes in potential-gradient in summer may be due largely to changes in resistivity, while in winter there may be appreciable changes due to changes in nucleation.

If the residual influence of gross particles is neglected and a regression equation is formed between potential-gradient, resistivity, and nuclei,

$$\delta X = a\delta R + b\delta N,$$

the correlation coefficient between the two sides of this equation is 0·73 in summer, 0·65 in winter, and 0·74 for the year. These are not of considerable significance, and show that only about 50 per cent of the changes in potential-gradient may be accounted for by local changes in the concentrations of atmospheric particles and nuclei.

Approximate values of the coefficients *a* and *b* in the equation may be determined. On substituting the values of the means and standard deviations we find

$$X = 0{\cdot}2 \times 10^{-16} R + 0{\cdot}3 \times 10^{-4} N + 1{\cdot}4 \pm 1{\cdot}2\, Ca \qquad \text{......(4).}$$

The residual term is larger than the standard value of the casual term and may not therefore be neglected. It is of the same order as that of potential-gradient at sea at 15 h.; it represents the best available approximation to the potential-gradient which would have been found at Kew at 15 h. if the atmosphere had been free from pollution.

§8. THEORETICAL CONSIDERATIONS

The outstanding results of the statistical comparison are that: (1) The resistivity of the air at Kew depends on the concentration of gross particles and of condensation nuclei; and (2) the potential-gradient is related to resistivity and also to the concentration of nuclei. No direct influence of the gross particles on potential-gradient is apparent.

Resistivity. The usual way of regarding the association of resistivity with the amount of pollution is to say that the conductivity is due almost entirely to the small ions in the air. The number of small ions varies inversely as the number of condensation nuclei; for the rate at which small ions are produced is nearly constant, and the life of a small ion is terminated by collision with a nucleus, charged or uncharged. Thus the expectation of life of a small ion is inversely proportional to the number of nuclei, and it follows that resistivity is proportional to the number of nuclei. Moreover, since increasing pollution is associated with increased concentration of nuclei, resistivity is also likely to be proportional to the number of gross particles.

Conclusion (1) above is in general agreement with these ideas except that the statistics suggest that gross particles play an active part in determining the resistivity. The natural assumption to make is that some of the small ions collide with the gross particles and combine with them.

When nuclei are plentiful the equation of electrical balance between the number of small ions and the number of nuclei may be written(15)

$$q = 0{\cdot}61 \eta N n,$$

where q is the rate of production of small ions;

η the recombination coefficient between small ions and large ions;

N the total number of nuclei, charged and uncharged;

and n the number of small ions.

The factor 0·61 is adopted from the work of Nolan and O'Brolchain. It will be noticed that if the small ions had combined with equal readiness with large ions of opposite sign and with uncharged nuclei, and if the ions of either sign and the uncharged nuclei had been equally plentiful, this factor would have been $\frac{2}{3}$.

In order to allow for the possibility of collisions between small ions and gross
P particles we may add to this equation a term βPn, where P is the number of gross
β particles and β may be taken to represent a recombination coefficient between small ions and gross particles. Thus we write

$$q = 0{\cdot}61\eta Nn + \beta Pn \qquad \text{......(5)}.$$

Now the resistivity R is given by

$$R^{-1} = e\,(nk + N'/K),$$

k where k is the average mobility of the small ions;

N', K N' is the number of large ions and K their average mobility;

e and e is the electronic charge per ion, $15{\cdot}9 \times 10^{20}$ coulombs.

At Kew Observatory the average values of n and N' are of the order of 300 and 10,000 respectively. The value of k is about 1·3 cm./sec. per V./cm., that of K about 1/3000 cm./sec. per V./cm. Thus $N'K$ is small compared with nk, and we may write

$$R^{-1} = enk = 20{\cdot}7 \times 10^{-20} n \qquad \text{......(6)}.$$

Hence from (5) and (6)

$$10^{-18} R = 2{\cdot}9\eta\, N/q + 4{\cdot}8\beta P/q \qquad \text{......(7)}.$$

Nothing is known as to the value of q at Kew or as to its variations. Let us suppose that if q is not a constant the fluctuations in q are independent of those of N and P. For the present we are only concerned with averages, and we note that equation (7) is of the same type as equation (1) which was derived from the observations, viz.,

$$10^{-12} R = 0{\cdot}77N + 37P \qquad \text{......(1)}.$$

Comparing coefficients and adopting the value of η found (15) at Dublin, $5{\cdot}7 \times 10^{-6}$, we deduce

$$q = 21 \text{ and } \beta = 17 \times 10^{-6}.$$

This value of q is improbably high. Perhaps we have taken too high an estimate for η.

For the ratio of the combination coefficients we are not dependent on the value of η or on the value of q at Kew. Equations (1) and (7) give

$$\beta/0{\cdot}61\eta = 37/0{\cdot}77 = 48.$$

This means that when nuclei and particles are equally numerous, the risk of a recombination between a small ion and a gross particle is about 50 times as great as the risk of a recombination between a small ion and a nucleus.

Now in estimating the risk of collision we may ignore the velocity of the larger particles, since they are very heavy compared with the small ions. Only the movements of small ions need be considered, and the risk of collision is therefore proportional to the area of the obstacle. Accepting the estimates 4×10^{-5} cm. and 4×10^{-6} cm. for the radii of particles (16) and nuclei (17) respectively, we find that the areas are in the ratio 100 : 1. That the recombination coefficients should be in the ratio 50 : 1 is quite consistent, for it is possible that the proportion of combinations to collisions is lower with the large particles than with nuclei.

Potential-gradient. Potential-gradient may be regarded from two points of view, the statical and dynamical. According to electrostatics, if the charges in the atmosphere are distributed in uniform horizontal layers, then the potential-gradient at any point is proportional to the total charge above it. Hence we infer from the results of the statistical investigation that the total electric charge in the atmosphere increases when resistivity near the ground increases, and also, for constant resistivity, when the number of nuclei near the ground increases.

On the other hand, from the point of view of electrodynamics we note that the air-earth current I is numerically equal to the quotient of potential-gradient by resistivity. Hence from (4)

$$I = X/R = 0{\cdot}2 \times 10^{-16} + 0{\cdot}3 \times 10^{-4}\, N/R + 1{\cdot}4/R.$$

Thus the current decreases when the local resistivity increases, the number of nuclei remaining constant. This would be expected on the assumption that the voltage of the upper atmosphere is constant and the total resistance at all heights, $\int R\, dz$, increases with the local resistivity. The significance of the term in N/R in the last equation is however not at all obvious. But the details of the mechanism of the air-earth current, the parts played by eddy movements and by conductivity, are not known, and so the discussion of the observations under review cannot be carried further at present. More light will be thrown on the subject when observations of volume-charge are available at Kew.

§9. ACKNOWLEDGMENTS

I am indebted to Dr G. C. Simpson, C.B., F.R.S., Director of the Meteorological Office, for his interest and for permission to publish the work. I wish to express my best thanks to Dr F. J. W. Whipple, Sc.D., F.Inst.P., Superintendent of Kew Observatory, for his interest throughout the course of the investigation, and for his advice and generous help in the discussion of the results. My thanks are also due to Mr P. A. Sheppard, B.Sc., who has attended to the observational work since May 1929, and to Mr B. V. Bishop for assistance with the computations.

REFERENCES

(1) S. J. Mauchly. *Physic. Rev.* **18**, 161, 477 (1921); *Washington Res. Dep. Terr. Mag., Carnegie Inst.* **5**, 385 (1926).
(2) K. Hoffmann. *Beitr. Physik Atmos., Leipzig,* **11**, 1 (1923).
(3) S. J. Mauchly. *Terr. Mag.* **28**, 68 (1923).
(4) F. J. W. Whipple. *Q. J. R. Met. Soc.* **55**, 1 (1929).
(5) C. Chree and R. E. Watson. *Proc. R. S.* **105**, 311 (1924).
(6) F. J. W. Whipple. *Q. J. R. Met. Soc.* **55**, 351 (1929).
(7) G. R. Wait. *Terr. Mag.* **32**, 31 (1927).
(8) G. Builder. *Terr. Mag.* **34**, 281 (1929).
(9) R. E. Watson. *Geo. Mem.*, No. 45, London, 1929.

(10) J. Aitken. *Coll. Sci. Papers*, p. 236 (1923).

(11) J. S. Owens. *Advis. Comm. Atmos. Poll.*, p. 34 (1922).

(12) H. L. Wright. *Geo. Mem.*, No. 57, London, 1932.

(13) H.M. Stationery Office, London.

(14) F. J. W. Whipple. *Phil. Mag.* (i), 378 (1926).

(15) J. J. Nolan and C. O'Brolchain. *Proc. Roy. Irish Acad.* **38** A4, 40 (1929).

(16) H. L. Wright. *Loc. cit.*; see also *Advis. Comm. on Atmos. Poll.* pp. 36–8 (1923) for measurements of maximum diameters of particles under a microscope.

(17) Sir J. J. Thomson. *Conduction of Electricity through Gases*, **1**, 189 (1928); J. J. Nolan, *Q. J. R. Met. Soc.* **55**, 173 (1929).

DISCUSSION

Dr F. J. W. Whipple. I am glad to have this opportunity to express my appreciation of the work done by the author in analysing the observations made at Kew Observatory of the numbers of particles in the air and of the conductivity and potential-gradient. It happens only too frequently that such observations, published or unpublished, accumulate without analysis.

One of the most striking developments in the paper is the demonstration that the resistivity of the air depends on the number of gross particles as well as on the number of nuclei. I mentioned this discovery of the author's some time ago and Prof. J. J. Nolan then declared that it was not in accordance with his observations in Ireland. Further comparisons are called for.

The explanation given by the author, that the gross particles are 100 times as effective as the nuclei in reducing the numbers of small ions by collision, may be correct, but we do not know that such collisions would destroy small ions. An alternative explanation is that the large ions associated with pollution are themselves bigger than those to be found in clean air. In fact there is no reason to suppose that the η of equation (5) is constant, and the factor to which the value 0·61 is assigned is probably variable.

The suggestion in figure 5 of the paper, that with resistivity zero the potential-gradient would be nearly 1 V./cm., invites comment. One can only surmise that the graph should bend sharply towards the origin. Unfortunately observations at Kew Observatory with air so pure that the resistivity falls below $10^{16}\,\Omega$.-cm. are too rare to provide good averages. The investigation will have to be extended to include observations in other parts of the country.

Prof. A. O. Rankine pointed out that according to the author the conductivity of the air appears to decrease as the number of nuclei increases—a surprising conclusion.

Author's reply. With regard to the apparent ineffectiveness of gross particles on the concentration of small ions in Ireland (reference 15), it is to be noted that variations in the function $q/0{\cdot}61nN$ may not be expected to show any conspicuous dependence on P, but rather on the ratio P/N. This is evident from equation (5) which may be written in the form $q/0{\cdot}61nN = \eta + \beta P/0{\cdot}61N$. Dr Whipple's statement that η is variable cannot, I think, be gainsaid, and to examine the extent of its variations is a problem for the future. Zero resistivity in air is difficult to imagine, but the resistivity at sea is about $0{\cdot}7 \times 10^{16}$ Ω.-cm., and the potential-gradient is of the order of 1 V./cm. These coordinates would lie on the graph drawn in figure 5, and so it would seem that if the graph eventually bends towards the origin it does so at a stage when lower resistivities than those normally experienced at sea are reached. That the graph drawn in figure 5 fails to pass through the origin is the geometrical illustration of the residual term in equation (4), though the magnitude of this term is not quite the same as that indicated in figure 5. It may be that we have to consider this as representing a universal term in the potential-gradient, uniform all over the world at a given instant.

The clue to the difficulty raised by Prof. Rankine is to be found in the second paragraph of § 8. I should perhaps have emphasized early in § 3 that the conductivity is preponderantly due to small ions owing to their extremely high mobility, and as a small ion is destroyed by collision with a nucleus, becoming in fact a large ion, it follows that the greater the number of nuclei the less the chance of survival of small ions, and hence the less the conductivity. Thus conductivity decreases with increasing concentration of nuclei.

621.352.12

THE TEMPERATURE COEFFICIENT OF THE SATURATED WESTON CELL

By P. VIGOUREUX and S. WATTS of the National
Physical Laboratory

Communicated by Dr E. H. Rayner, October 17, 1932. *Read January* 20, 1933.

ABSTRACT. The effect of temperature on the electromotive force and on the performance of acid Weston cells has been studied from − 24 to + 40° C. The e.m.f. reached a maximum at about 3°, and at − 20° it was just over a millivolt less than the maximum. The cells behaved satisfactorily at − 16°, but at − 18° freezing took place gradually and was accompanied by a rapid decrease in e.m.f. At − 24° the electrolyte had completely solidified, and the e.m.f. was about 12 millivolts lower than the maximum. The frozen cells resumed their normal behaviour when kept at room temperature for about a day. Cooling increased the internal resistance of the cells. The e.m.f. temperature formula in common use does not hold below 0°, but a slightly different formula has been obtained, valid between − 20° and + 40°.

§ 1. PREVIOUS INVESTIGATIONS

The most extensive investigation of the temperature coefficient of Weston cells is due to Wolff*, who gave for the change of e.m.f. between 0° and 40° the formula

$$\Delta e = -40{\cdot}75\,(t-20) - 0{\cdot}944\,(t-20)^2 + 0{\cdot}098\,(t-20)^3$$

Δe, t in which Δe is the divergence in microvolts from the e.m.f. at 20°, and t is the temperature. It has subsequently been shown that acidity of the electrolyte does not affect the temperature coefficient to an appreciable extent†, and that the formula‡

$$\Delta e = -40{\cdot}6\,(t-20) - 0{\cdot}95\,(t-20)^2 + 0{\cdot}01\,(t-20)^3$$

expresses to a high order of accuracy the variation of electromotive force with temperature between the above-mentioned limits.

§ 2. DESCRIPTION OF CELLS EXAMINED

Twelve cells made in March 1932 were subjected to the temperature cycles. The cadmium amalgam constituting the negative pole contained only 6 per cent of cadmium in eight of the cells, but the usual 10 per cent in the other four. The reason for using a lower cadmium-content in some of the cells is that, for stability, both the solid and the liquid phases of the amalgam must be present together. At temperatures below − 10° C. the solid phase only of a 10-per-cent amalgam would be present, if extrapolation of experimental results from 0° downwards is valid*, whereas a 6-per-cent amalgam would secure stability only between − 35° and + 28°. Experiment subsequently showed that the 10-per-cent amalgam, contrary to expectations, behaved satisfactorily down to − 20°, but the 6-per-cent amalgam acted according to prediction, and gave abnormal values of e.m.f. at and above 30°.

---

* *Bull. Bur. Stand.* 5, 309 (1908).

† *Researches Electrotech. Lab.* No. 88 (1921).

‡ London Conference, 1908.

In addition to the twelve cells subjected to the temperature test, six made in 1928 were connected permanently in parallel and used as comparison cells, and six made in 1929 were used individually as a check on the constancy of the comparison group. The solvent for the electrolyte of all the cells was sulphuric acid of decinormal strength.

Twelve cells, it might be thought, were hardly sufficient for the investigation, but the experience of many years acquired at the National Physical Laboratory, as well as the behaviour of the cells during the investigation, justified our views as to the stability and repetition of acid cells. At temperatures above 28° we could, it is true, use only the results obtained with the four cells containing 10-per-cent amalgam, but the exploration of that part of the range was only a verification of work often repeated, whereas the interest of the investigation lay chiefly with temperatures below 0°, at which the behaviour of standard cells had not as yet, as far as we are aware, been studied.

§ 3. EXPERIMENTAL DETAILS

A refrigerator, the tank of which contained a few hectolitres of a mixture of paraffin and machine oils kept constantly stirred, provided the required low temperatures. The twelve test cells were placed in a metal trough full of paraffin oil and provided with a heating resistance and a toluene thermostat. The trough could be lowered into the oil of the refrigerator tank. Stirring was effected by blowing dry air through small holes in a lead pipe resting on the bottom of the trough. By starting and stopping the refrigerator at intervals, it was easy to maintain in the trough a temperature constant to 0·05° at all points between − 24° and 5°. The comparison and reference cells were in an oil bath maintained at 20°. Mercury thermometers were used in both baths.

A Tinsley potentiometer giving single microvolts between successive studs of the last dial measured the difference in e.m.f. between each of the twelve test cells and the comparison group, and between each of the six reference cells and the comparison group. When the cells were all at 20° the sensitivity as read on the galvanometer was about 3 mm. for 10 μV. At − 21° it was only about 0·8 mm., but even this was sufficient.

The time required to lower the temperature of the cells by 20° was about two hours. When the cells had reached the required temperature, half an hour was allowed to elapse and the eighteen measurements were made; about twenty minutes later, another set of readings was taken. It will be seen from table 1 that the two

---

* *Dict. of App. Phys.* **2**, 264.

Table 1. Measurements of the e.m.f. of twelve standard cells

Date, 1932	Summer time	Temperature of cells under test	6-per-cent amalgam			10-per-cent amalgam		
			e.m.f. of test cells minus e.m.f. of 1928 cells at 20° (μV.)	e.m.f. of test cells minus e.m.f. of test cells at 20° (μV.)	No. of cells used for the mean	e.m.f. of test cells minus e.m.f. of 1928 cells at 20° (μV.)	e.m.f. of test cells minus e.m.f. of test cells at 20° (μV.)	No. of cells used for the mean
April 26	—	20	+ 7	0	8	+ 7	0	4
May 3	—	− 4·1	+ 285	+ 278	8	—	—	—
	—	− 4·1	+ 279	+ 272	8	+ 284	+ 277	4
	—	− 10·2	+ 64	+ 57	8	+ 67	+ 60	4
	—	− 10·2	+ 62	+ 55	8	+ 64	+ 57	4
	16.30	− 15·35	− 249	− 256	8	− 246	− 253	4
	17.00	− 14·95	− 224	− 231	8	− 221	− 228	4
May 4	10.20	− 0·92	+ 341	+ 334	8	+ 344	+ 337	4
	10.50	− 0·95	+ 343	+ 336	8	+ 344	+ 337	4
	11.40	0·0	+ 354	+ 347	8	+ 354	+ 347	4
	12.20	0·0	+ 354	+ 347	8	+ 355	+ 348	4
	13.15	+ 1·0	+ 362	+ 355	8	+ 365	+ 358	4
	13.55	+ 1·0	+ 362	+ 355	8	+ 364	+ 357	4
	16.40	− 19·95	− 653	− 660	5	− 660	− 667	2
	17.15	− 19·9	− 652	− 659	5	− 663	− 670	2
May 5	10.45	− 1·75	+ 326	+ 319	8	+ 334	+ 327	4
	11.10	− 1·75	+ 325	+ 318	8	+ 332	+ 325	4
	11.45	0·0	+ 348	+ 341	8	+ 355	+ 348	4
	12.10	0·0	+ 348	+ 341	8	+ 355	+ 348	4
	12.50	+ 1·95	+ 363	+ 356	8	+ 368	+ 361	4
	13.40	+ 2·03	+ 364	+ 357	8	+ 370	+ 363	4
	14.15	+ 2·95	+ 369	+ 362	8	+ 381	+ 374	4
	14.50	+ 2·95	+ 367	+ 360	8	+ 373	+ 366	4
	15.25	+ 3·9	+ 365	+ 358	8	+ 372	+ 365	4
	15.55	+ 3·95	+ 366	+ 359	8	+ 371	+ 364	4
	16.30	+ 4·9	+ 362	+ 355	8	+ 368	+ 361	4
	17.00	+ 4·9	+ 361	+ 354	8	+ 369	+ 362	4
May 6	10.45	+ 20·0	+ 5	—	8	+ 6	—	4
	11.20	+ 20·0	+ 7	0	8	+ 7	0	4
	14.25	− 18·05	− 482	− 489	8	− 473	− 480	4
	15.35	− 18·0	− 483	− 490	8	− 475	− 482	4
	16.50	− 19·1	− 583	− 590	8	− 566	− 573	3
	17.30	− 19·3	− 607	− 614	7	− 605	− 612	3
May 7	10.50	− 19·0	− 579	− 586	3	− 581	− 588	2
	12.15	− 20·05	− 680	− 687	2	− 664	− 671	1
	12.45	− 20·05	− 671	− 678	1	− 668	− 675	1
May 9	11.10	− 7·65	+ 187	+ 180	8	+ 188	+ 181	4
	12.00	− 7·7	+ 183	+ 176	8	+ 190	+ 183	4
	16.15	− 21·0	− 796	− 803	1	The other 11 cells gave values between − 2000 and − 9000 μV.		
	17.00	− 21·15	e.m.f. was decreasing rapidly. Results varied between − 3000 and − 9000 μV.					
May 10	14.30	− 24·0	− 11000	—	8	− 12000	—	4
	15.10	− 24·0	− 11000	—	8	− 12000	—	4
	17.20	+ 20·0	− 99	—	8	− 52	—	4
	18.20	+ 20·0	− 84	—	8	− 50	—	4

Table 1. Measurements of the e.m.f. of twelve standard cells (*continued*)

Date, 1932	Summer time	Temperature of cells under test	6-per-cent amalgam			10-per-cent amalgam		
			e.m.f. of test cells minus e.m.f. of 1928 cells at 20° (μV.)	e.m.f. of test cells minus e.m.f. of test cells at 20° (μV.)	No. of cells used for the mean	e.m.f. of test cells minus e.m.f. of 1928 cells at 20° (μV.)	e.m.f. of test cells minus e.m.f. of test cells at 20° (μV.)	No. of cells used for the mean
May 11	10.00	+ 20·0	− 21	—	8	− 6	—	4
	10.45	+ 20·02	− 22	—	8	− 6	—	4
	15.15	− 18·1	− 526	− 506	6	− 500	− 494	4
	16.05	− 18·1	− 526	− 506	6	− 506	− 492	3
May 12	10.30	− 18·1	− 519	− 499	5	− 505	− 491	2
	12.30	+ 20·0	− 20	—	8	− 14	—	4
	14.00	+ 20·0	− 17	—	8	− 13	—	4
	16.30	− 16·1	− 352	− 335	8	− 339	− 326	4
May 13	11.00	− 16·1	− 335	− 335	8	− 324	− 330	4
	12.30	− 16·15	− 338	− 338	8	− 329	− 335	4
	14.30	− 16·15	− 337	− 337	8	− 326	− 332	4
May 14	13.00	+ 20·0	+ 1	—	8	+ 6	—	4
May 17	17.00	20·0	− 2	—	8	+ 9	—	4
May 19	16.30	20·0	− 1	—	8	+ 9	—	4
May 26	—	20·0	+ 4	—	8	+ 10	—	4
May 30	—	20·0	+ 6	—	8	+ 10	—	4
June 9	—	20·0	+ 6	—	8	+ 9	—	4
June 18	—	20·0	+ 6	—	8	+ 7	—	4
July 8	13.45	20·0	+ 6	—	8	+ 8	—	4
	14.55	20·0	+ 5	—	8	+ 9	—	4
	16.40	26·0	− 264	− 271	8	− 263	− 272	4
	17.50	26·0	− 266	− 273	8	− 264	− 273	4
July 9	10.50	20·0	+ 8	—	8	+ 8	—	4
	12.00	20·0	+ 8	—	8	+ 10	—	4
July 11	11.00	30·0	− 492	Abnormal	—	− 474	− 482	4
	12.00	30·0	—	,,	—	− 479	− 487	4
	13.45	34·0	—	,,	—	− 717	− 722	4
	14.30	34·0	—	,,	—	− 717	− 722	4
	16.00	36·97	—	,,	—	− 910	− 913	4
	16.45	37·0	—	,,	—	− 906	− 909	4
July 12	11.20	20·0	+ 5	—	8	+ 2	—	4
	12.30	20·0	+ 7	—	8	+ 6	—	4
	14.55	40·0	—	Abnormal	—	− 1116	− 1120	4
	15.50	40·0	—	,,	—	− 1113	− 1118	4
	16.45	40·0	—	,,	—	− 1109	− 1114	4
July 13	11.15	20·0	+ 5	—	8	+ 5	—	4
	12.30	20·0	+ 5	—	8	+ 5	—	4
July 14	10.45	20·0	+ 6	—	8	+ 6	—	4
	11.35	20·0	+ 6	—	8	+ 5	—	4
	12.35	22·0	− 78	− 84	8	− 78	− 83	4
	14.30	22·0	− 77	− 83	8	− 78	− 83	4
July 15	10.30	17·41	+ 103	+ 96	8	+ 104	+ 96	4
	12.00	17·54	+ 100	+ 93	8	+ 100	+ 92	4
	13.45	20·0	+ 8	—	8	+ 8	—	4
	14.45	20·0	+ 7	—	8	+ 8	—	4

sets were always in excellent agreement, indicating that the lag was very small. It was consequently possible to complete the low-temperature investigation in ten days, during which 736 individual measurements were made; they were spread over sixteen different temperatures between − 24° and 5°. In addition, the test cells were often raised to 20°, and measured at that temperature. A similar procedure was observed for measurements at room temperature and above.

§ 4. BEHAVIOUR OF THE CELLS

The summary of results in table 2 shows that the electromotive force reaches a maximum at about 3°; the curve connecting electromotive force and temperature resembles a parabola with vertex upwards and axis perpendicular to the temperature axis as in figure 1. Down to − 16° the electromotive force reached the value expected from the curve in less than an hour, and suffered no subsequent change. When the cells were cooled to − 18°, the e.m.f. also reached the expected value within an hour, after which it would remain constant for several hours; but then one of the twelve cells would suffer a gradual decrease in e.m.f. Then another cell, and then a third, would behave in a similar manner. It was found on examination that the electrolyte of the cells undergoing the abnormal decrease

Table 2. Relation between e.m.f. and temperature

Temperature (° C.)	Experiment*		Formula − experiment (μV.)	
	Actual points	Best curve	Formula in general use	Formula proposed
− 20	− 672	− 674	139	− 3
− 19	− 582	− 577	124	+ 2
− 18	− 487	− 485	108	+ 3
− 16	− 324	− 313	76	0
− 15	− 230	− 233	62	− 2
− 10	68	75	18	− 6
− 7·7	179	174	9	+ 3
− 4·1	276	276	11	+ 5
− 1·75	322	322	10	+ 5
− 1	335	333	7	+ 5
0	346	346	6	+ 4
1	356	355	5	+ 2
2	359	361	3	+ 1
3	365	363	3	0
4	362	362	4	0
5	358	358	4	− 1
10	—	301	0	− 5
14	—	205	2	− 3
17·5	92	92	3	0
20	0	0	0	0
22	− 83	− 83	− 2	+ 2
26	− 272	− 272	− 4	+ 5
30	− 484	− 484	− 7	+ 5
34	− 722	− 722	− 5	+ 6
37	− 912	− 912	− 3	0
40	− 1118	− 1118	+ 6	0

* Excess in microvolts of the e.m.f. over the e.m.f. at 20°.

was gradually becoming solidified. The process was slow at − 18°, for after twenty hours at that temperature five out of the twelve cells were partly frozen, but it is probable that the electrolyte in all of them would have become solidified had the experiment been continued. A similar test was tried at − 16°, but the cells behaved normally during its twenty-four hours' duration. We conclude that Weston cells, or at least those made with solvent of decinormal acidity, are satisfactory at − 16°.

The process of solidification is much faster when the temperature is lowered to − 19° or − 20° instead of to − 18° only; but even at − 21° one of the cells behaved normally for about half an hour. In evaluating the mean electromotive force at any temperature, only those cells were considered whose behaviour was normal; above − 18° results on all the cells were used, but below this temperature the cells which exhibited a continuous decrease in e.m.f. were, of course, not taken into account.

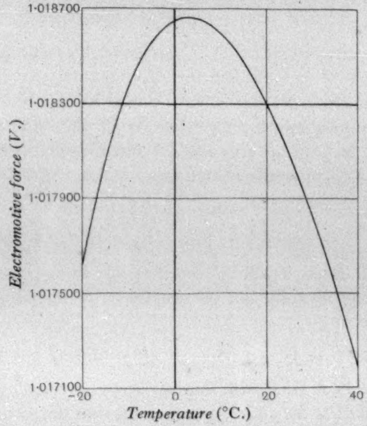


Figure 1. Relation between the electromotive force of the Weston (saturated) cell and its temperature.

After the freezing to − 24°, an undoubtedly severe treatment, the bath was warmed, and in an hour the temperature had reached + 20°. Half an hour later the 6-per-cent amalgam cells still gave about 100 μV., and the 10-per-cent about 50 μV., below the normal value. This, and the subsequent behaviour, are shown in table 1. Recovery was complete in about a week.

Want of space precludes us from giving here the individual results from which table 1 was constructed, but it should be mentioned that the behaviour of the cells was not so uniform that they all had the same value at all temperatures; nevertheless the maximum and mean deviations from the mean, even at − 18°, did not exceed 22 and 11 μV. respectively, so that the mean of the twelve cells may be regarded as a fair average, of accuracy 5 μV.

§ 5. DERIVATION OF A FORMULA

The temperatures in table 1 are not all in round numbers, but it is easy to obtain the first two columns of table 2 by plotting a graph and applying the small corrections required. The figures in the second column are the means of the values of the 6-per-cent and 10-per-cent amalgam cells for all temperatures below 30°, and of the latter only for higher temperatures. A curve drawn on a large scale yielded the figures in column 3, which agree closely with the experimental points. The formula in general use to-day, viz.,

$$\Delta e = -40{\cdot}6\,(t-20) - 0{\cdot}95\,(t-20)^2 + 0{\cdot}01\,(t-20)^3,$$

does not agree with experiment below 0°, as shown by column 4, which gives the differences between that formula and the experimental curve. A cubic formula seems inadequate to represent the actual state of things, but by going one step further it is possible to obtain for the whole range the same accuracy which the cubic formula gives for the positive half. From the figures in the last column, which are differences between the formula

$$\Delta e = -39{\cdot}39\,(t-20) - 0{\cdot}903\,(t-20)^2 \\ + 0{\cdot}0066\,(t-20)^3 - 1{\cdot}5 \times 10^{-4}\,(t-20)^4$$

and the experimental curve, it will be seen that only in one case is the discrepancy as large as $6\,\mu$V. The formula can be simplified by referring the temperatures to 3°, thus

$$\Delta e = 363 - 1{\cdot}5\,(t-3)^2 + 1{\cdot}68 \times 10^{-2}\,(t-3)^3 - 1{\cdot}5 \times 10^{-4}\,(t-3)^4.$$

Other formulae have been tried with maxima at 3·2, 3·3 and 3·4°, but they do not give as good agreement as the above, and it seems that the maximum e.m.f. occurs very close indeed to 3°, which might, for some purposes, prove a convenient temperature for the standardization and comparison of cells.

§ 6. DISCUSSION OF RESULTS

The temperature of maximum electromotive force determined by this investigation is in exact agreement with the results of Wolff*. Although it is possible that the variations of electromotive force with temperature depend on other factors besides the concentration of the electrolyte, the negligible temperature coefficient of unsaturated cells, indicating as it does that the influence of such factors is very small, suggests that the minimum solubility of cadmium sulphate, whether in water or decinormal sulphuric acid, occurs at a temperature of 3°. This result is in agreement with the solubility determinations of Mylius and Funk† and of von Steinwehr‡, but at variance with those of Cohen and Wolters§, who assign − 9° to the point of minimum solubility.

---

* *Loc. cit.*

† *Ber. deuts. chem. Ges.* **30**, 824 (1897).

‡ *Z. phys. Chem.* **88**, 229 (1914).

§ *Z. phys. Chem.* **96**, 253 (1920).

The phenomena observed at low temperatures can be explained from the freezing-point and solubility data* for cadmium sulphate. The solubility curve of $3CdSO_4 . 8H_2O$ meets the freezing-point curve at − 17°, when a solid of composition $CdSO_4 + 14{\cdot}5H_2O$ is precipitated. The cell can, therefore, be expected to function satisfactorily above this temperature, and probably, with suitable amalgams, up to 74·5°, at which temperature another transformation takes place. The slow rate of solidification at temperatures above − 19° might be caused by the formation of the metastable $CdSO_4 . 7H_2O$, which would lower the temperature of solidification of the solution, before it gradually suffered transformation into the stable salt $3CdSO_4 . 8H_2O$.

§ 7. INTERNAL RESISTANCE OF CELLS

An approximation to the internal resistance was obtained by observing the sensitivity of the potentiometer at various temperatures. The calibration was effected by replacing the cells by a resistance box. The figures below, representative of the values obtained, are only a rough approximation. The small resistance of the six comparison cells has been allowed for where necessary.

Temperature (° C.)	20	5	0	− 10	− 20	− 24 (completely frozen)
Average internal resistance (Ω.)	800	850	1700	2500	5000	40,000

The average resistance of the reference cells made in 1929 seems to lie between 500 and 600 Ω.

§ 8. ACKNOWLEDGMENTS

We wish to thank the Superintendent of the Physics Department of the National Physical Laboratory, Dr Kaye, who gave us facilities for carrying out the low temperature work in his department; the several members of his staff for their help, and Dr E. H. Rayner, Superintendent of the Electricity Department, who instigated the research, for his encouragement throughout the investigation.

---

* Mylius and Funk, *loc. cit.*

538.71

A NEW APPARATUS FOR THE MEASUREMENT OF THE EARTH'S MAGNETIC FIELD

By L. F. BATES, Ph.D., Reader in Physics, University College, London

Received October 18, 1932. *Read December* 16, 1932.

ABSTRACT. A new method for the determination of the horizontal and vertical components of the earth's magnetic field is described. A small cylinder of mu-metal is wound with fine wire whose ends are connected to wires forming a torsional suspension. This cylinder is placed with its centre at the mid-point of a Helmholtz coil system whose axis is adjusted to coincide with the direction of the component of the earth's field which is to be measured, the suspension being perpendicular to the component. The current through the coil system can be adjusted so that there is no deflection of the suspended cylinder when the current in the solenoid wound upon it is reversed, in which case the calculated field produced by the coils is equal to the required component. The sources of error peculiar to the method are examined and their elimination is discussed. It is shown that measurements of high accuracy are possible.

§ 1. INTRODUCTION

For a complete knowledge of the earth's magnetic field in a particular region it is necessary to determine the magnitudes of the horizontal and vertical components of that field. The horizontal component may be accurately found by several methods, the most rapid being that of Schuster and F. E. Smith*, of which a simple modification was recently described by the writer†. The vertical component is usually calculated from a knowledge of the horizontal component and the angle of dip, the latter being generally determined with an earth inductor in series with a galvanometer.

F. E. Smith‡ has outlined a direct method for the measurement of the vertical component. A small coil is rotated with constant frequency about a horizontal diameter in the magnetic meridian, the ends of the coil being connected to a vibration galvanometer. The vertical field acting on the rotating coil may be annulled by passing a current through a Helmholtz galvanometer coil system, whose axis is vertical and whose mid-point coincides with the mid-point of the rotating coil. When no current flows through the galvanometer, the current in the coil system is exactly that required to neutralize the vertical component of the earth's field, so that this component can be calculated from the dimensions of the coil system and the magnitude of the current.

---

* F. E. Smith, *Phil. Trans. R. S.* A **223**, 175 (1922).

† L. F. Bates, *J. Sci. Inst.* **8**, 324 (1931).

‡ F. E. Smith, *loc. cit.* 177.

The writer was not aware that any other methods had been reported until his work with the apparatus described below had been completed and the following account—which has been left entirely unaltered—had been written. His attention was then drawn to a method described and tested with customary precision by the late Dr D. W. Dye*.

In Dye's method a very light coil is suspended so that it may rotate about a horizontal axis in the magnetic meridian, the plane of the coil being in the meridian. When supplied with alternating current of the resonant frequency, the coil vibrates in a manner similar to a coil-type vibration galvanometer under the influence of the vertical component of the earth's field. The mid-point of the coil is situated at the mid-point of a Helmholtz coil system whose axis is vertical.

A current supplied to the Helmholtz coil system is adjusted until the resonance vibrations disappear, when the vertical component of the earth's field is exactly neutralized in the region occupied by the vibrating coil. The vertical component is calculated from a knowledge of the current and the dimensions of the coil system. Using the refinements possible at the National Physical Laboratory, Dye thus measured the vertical component with an accuracy of one part in twenty thousand.

The apparatus now to be described enables both the horizontal and the vertical components to be rapidly determined with considerable accuracy. With the present construction the mean error of a determination is of the order of one part in a thousand, but with further refinements greater accuracy is obtainable.

§ 2. THEORY OF THE METHOD

The method of determining the vertical component, for which the apparatus was primarily designed, will be first described. In figure 1*a*, *XX* represents a small cylinder of mu-metal, chosen because of its very high permeability in low fields, on which is wound a solenoid of thin insulated wire. The ends of the wire are brought to *B* and *C*, where they are soldered to the ends of two fine phosphor-bronze galvanometer suspensions, *AB* and *CD*. The whole system is then mounted so that *AD* lies horizontally and in the magnetic meridian, whilst the axis of *XX* is adjusted to be horizontal and perpendicular to the line *AD*.

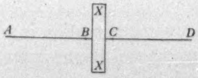


Figure 1*a*.

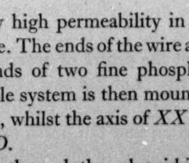


Figure 1*b*.

The passage of a current of a few milliamperes through the solenoid is sufficient to make the mu-metal, initially unmagnetized, a strong magnet. The vertical component of the earth's field acts upon this magnet, which tends to set with its magnetic axis vertical, and, consequently, the cylinder is deflected. The deflection is reversed by reversing the current through AD, and no deflection occurs if the vertical component of the earth's field is annulled.

---

* D. W. Dye, *Proc. R. S.* A **117**, 434 (1927).

The cylinder XX is mounted with its centre at the mid-point of a Helmholtz coil system whose axis is vertical, as shown in figure 2. A steady current is supplied to the coils, and by repeated adjustment of the current the vertical component of the earth's field may be entirely compensated in the region occupied by XX. When this condition is satisfied no deflection of XX occurs on reversing the current in AD. If exact compensation is not attained, the direction of the deflection of XX on reversal of the current in the solenoid will depend upon whether the compensating current is too large or too small to annul precisely the vertical component.

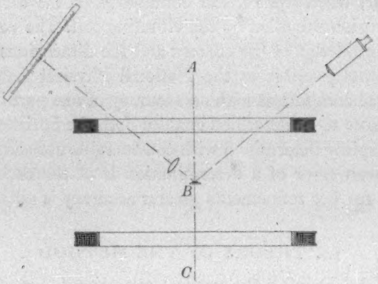


Figure 2. To measure the horizontal component: planes of coils are vertical with meridian on line ABC (i.e. the figure is plan view). To measure the vertical component: planes of coils are horizontal, with meridian perpendicular to plane of paper at B (i.e. the figure is an elevation). The magnet suspension is at B and perpendicular to plane of paper.

It is therefore possible to determine when exact compensation is attained, and hence, from a knowledge of the compensation current and the geometric constants of the Helmholtz coils, to calculate the magnitude of the vertical component of the earth's field. The several factors upon which the sensitiveness of the apparatus depends will now be described.

I, a Let I be the intensity of magnetization of the mu-metal cylinder, a its area of
l, m cross-section and l its length. Let the mass of the cylinder and solenoid be m, and
x suppose that the centre of gravity is at a distance x from the line about which the
θ cylinder turns. Let the axis of the cylinder make an angle θ with the horizontal,
and let the angle between the line from the centre of gravity perpendicular to the
ϕ axis of rotation and the horizontal be ϕ, when the magnetization is such that the
vertical component of the earth's field gives rise to forces in the directions shown
by the arrows in figure 1*b*.

Then, for equilibrium,

$$VIal\cos\theta + mgx\cos\phi = T\gamma \qquad \text{......(1)},$$

where V is the vertical component of the earth's field, T is the torsion constant of the system and γ is the angle through which it is twisted. The forces need not, of course, be coplanar. On reversing the magnetizing current the magnetic forces shown in figure 1*b* are reversed, the angles θ, ϕ and γ are decreased by $\delta\theta$, and we now have

V, T

γ

$\delta\theta$

$$-VIal\cos(\theta-\delta\theta)+mgx\cos(\phi-\delta\theta)=T(\gamma-\delta\theta) \qquad \text{......(2)}.$$

Subtracting (2) from (1), we have

$$VIal\{\cos\theta+\cos(\theta-\delta\theta)\}+mgx\{\cos\phi-\cos(\phi-\delta\theta)\}=T\delta\theta,$$

or, since $\delta\theta$ is small,

$$VIal\{2\cos\theta+\delta\theta\sin\theta\}-mgx\,\delta\theta\sin\phi=T\delta\theta,$$

whence

$$\delta\theta=2VIal\cos\theta/(T+mgx\sin\phi-VIal\sin\theta) \qquad \text{......(3)}.$$

Under the chosen experimental conditions the axis of the cylinder is practically horizontal, i.e. $\theta=0$. Also, when the vertical component of the earth's field is almost compensated, the field V must be replaced by a small field, δV, and we have

δV

$$\delta\theta=2\delta VIal/(T+mgx\sin\phi) \qquad \text{......(4)}.$$

The second term in the denominator of equation (4) may be made vanishingly small by decreasing x by the method described below, so that, in the limit, we may write

$$\delta\theta=2\delta VIal/T.$$

Hence the sensitiveness of the apparatus may be increased by increasing I—which means the use of solenoids of many turns—by increasing the dimensions of the cylinder, and, finally, by decreasing the torsion constant.

The value of I is limited by the magnitude of the current which may be passed through the solenoid together with the high demagnetization factor of the cylinder. The latter determines to some extent the dimensions of the cylinder, which are also limited by the mechanical strength of the suspension and by the fact that, unless the cylinder is small, it does not lie within the region over which the field produced by the Helmholtz coils can be regarded as constant. In fact, given that the position of the centre of gravity of the system has been properly adjusted, the torsion constant of the suspension is the factor which mainly governs the sensitiveness of the apparatus.

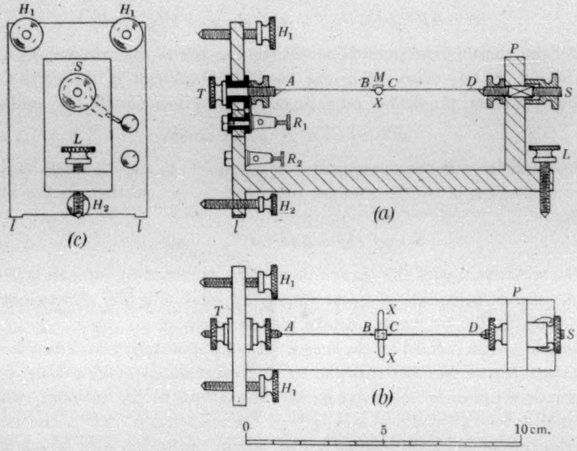
§ 3. EXPERIMENTAL DETAILS

Figures 3*a*, 3*b* and 3*c* represent respectively the elevation and plan views of the actual apparatus as arranged for the determination of the vertical component. The frame was constructed of non-magnetic brass. From figures 3*a* and 3*b*, it will be seen that the tension of the suspension could be adjusted by means of the screw *S*, which passes through a square hole in the brass pillar *P*.

The axis of the cylinder *XX* could be brought into a horizontal position by means of the torsion head *T*. The latter passed, as shown, through an ebonite bush, and it was in electrical communication with the insulated terminal, R_1. A second terminal, R_2, directly screwed to the brass support, allowed a current to be sent through the suspended system.

The electrical arrangements are shown in figure 4. A shunted millivoltmeter was used for measuring the current supplied to the Helmholtz coils. The latter were each of 30 turns of mean diameter 40 cm. Their centres were fixed (for convenience) 17·2 cm. apart in all experiments. The millivoltmeter was frequently calibrated and its shunt often changed so that the current determinations were free of bias.

The levelling screw L together with two projections l l, from the left-hand side of the base, figures 3*a* and 3*c*, enabled the suspension AD to be arranged as nearly horizontal as the slight sag, which was inevitably present, permitted. The dimensions of the frame were chosen with the view of making this sag as small as possible without greatly diminishing the sensitiveness.



Figures 3*a*, 3*b*, 3*c*.

In the diagrams a simple device for clamping the suspended system, when in transit, is not shown. Two pointers, attached to the base of the instrument vertically below the line AD, which were particularly helpful in fixing the position of the apparatus with respect to the magnetic meridian, are likewise not shown. A cardboard case provided with mica windows was used to shield the suspended system from the effects of air currents.

No electromagnetic or frictional damping devices were necessary to bring the suspended system to rest, as with a little practice it was easy to determine the equilibrium position when small oscillations persisted, and large oscillations were easily reduced by proper manipulation of the reversing switch shown in figure 4.

The cylinder XX was 1·5 cm. long and 1·4 mm. in diameter. These dimensions satisfied the conditions mentioned in the discussion of the theory of the method. Several such cylinders were wound and mounted, and experiments were made with those referred to as nos. 1, 2, 3 and 4 respectively. The solenoids on nos. 1 and 2 were wound by hand, the ends of the wire being looped as in figure 5, and then drawn taut. No. 1 was wound with 40 turns of no 36 s.w.g. copper wire, and no. 2 with 80 turns of no. 42 s.w.g. eureka wire. The wire was double-silk-covered and was passed through molten paraffin before being wound, in order to ensure more perfect insulation.

The solenoids on cylinders nos. 3 and 4 were wound on a lathe. A small hole was bored through the middle of each cylinder, and the solenoid was wound in two layers. The winding was started at the middle of the cylinder. Half of the cylinder to one side of the hole was completely wound and then the other half, the free end of the wire being passed through the hole. Special precautions were necessary to prevent short-circuiting of the solenoid where the wires passed through the hole. Cylinder no. 3 was wound with 160 turns of no. 42 s.w.g. eureka wire, and cylinder no. 4 with 140 turns of no. 36 s.w.g. copper wire.

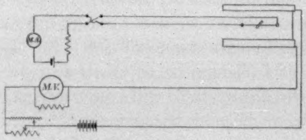


Figure 4.

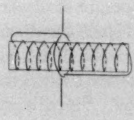


Figure 5.

On mounting the suspension it was generally found that the centre of gravity of the system was too far below the line AD. The centre of gravity was therefore raised by attaching small quantities of molten picein or of sealing wax to each end of the upper surface of the solenoid, until the period of torsional oscillation about AD became large. This was best done by loosening the screw S, lowering the system on to a support, and adding or removing wax with a hot copper wire. Cylinders nos. 3 and 4 were very symmetrically mounted and only required the addition of very small quantities of wax.

The phosphor-bronze galvanometer strip suspension which gave satisfactory results was 0·0025 × 0·0005 in. in cross-section, the lengths AB and CD being approximately those shown in figure 3. The mirror M was mounted with picein on the upper side of the cylinder, before adjustment of the centre of gravity. It was made from a small piece of microscope cover glass coated with platinum.

The optical arrangements for recording the rotation of the cylinder are shown in figure 2. The scale was usually conveniently placed about 50 cm. from the mirror M; this distance could, of course, be increased. A suspension was considered satisfactory if the reversal of a current of not more than 10 mA. in the solenoid produced a deflection of about 10 cm. on the scale when the vertical component of the earth's field was not compensated.

§ 4. SOURCES OF ERROR

The first possible source of error to be discussed is the effect of the current in *AD* upon the poles of the cylinder. For the purpose of calculation, we may look
i upon *AD* of figure 3*a* as a long straight wire carrying a current i. The pole strength of the mu-metal cylinder is Ia, and a force approximately equal to $(2i/\frac{1}{2}l)\ Ia$ will act on each pole. Hence the system experiences a couple of electromagnetic origin equal to $4iIa$. Since i and I always have the same sign, the sense of this couple is constant.

The effect of the current in *AD* will therefore be to cause a constant displacement of the cylinder, but it cannot affect the determination of the vertical component unless I varies in magnitude with the direction of the current in the solenoid. In the experiments described below, the maximum value of i was 30 mA., and l was 1·5 cm. Hence the maximum value of the couple was 0·008 Ial.

Thus, even if the numerical value of I changes by as much as 1 per cent on reversal of the current in the solenoid, the deflection $\delta\theta$ will only be proportional to 0·00008 Ial. Since it is easily possible to measure the compensating current to one part in 800, the limiting deflection due to uncompensated field is proportional to $V/800\ Ial$ or 0·0005 Ial. The error due to the lack of constancy of I can only become important when measurements are made to an accuracy of greater than one part in 10,000.

In any case, with a comparatively high field in the solenoid it is difficult to believe that the value of I can change by as much as 1 per cent on reversal. If, however, it is proved that the change is appreciable, then the error can be greatly reduced by running a wire parallel to and just below *AD*, so that the solenoid current passes along *AD* and returns through the lower wire, whose magnetic field will almost neutralize that of *AD* near the poles of the cylinder.

Another source of error arises when the line *AD* does not coincide with a horizontal line in the magnetic meridian passing through the centre of the cylinder. A slight displacement of *AD* from the meridian can easily be shown to give rise to very little error. A slight displacement from the horizontal, however, gives rise
α to serious error. For let *AD* make a small angle α with the horizontal. Then the horizontal component of the earth's field may be resolved into components,
H $H\cos\alpha$ and $H\sin\alpha$, respectively parallel and perpendicular to *AD*. The latter component will produce a couple approximately given by $H\sin\alpha\,.\,Ial$. If α is of the order of 1°, this couple is approximately 0·004 Ial, i.e. about eight times greater than the smallest measurable current difference. There is, fortunately, every reason why α should be very much less than 1° with an apparatus properly constructed and set up.

In any case the error may be avoided by taking a further value of the compensating current with the whole apparatus turned through 180° in a horizontal plane, when the direction of the couple due to the horizontal component of the earth's field will be reversed, while the vertical couple remains unchanged. This rotation is much facilitated by the provision of the pointers mentioned in an earlier section, care being taken that the centre of the cylinder is always placed in the same position with respect to the Helmholtz coils.

The most serious source of error arises if the axis of the coils is not strictly vertical. If measurements correct to 1 part in 1000 are required, a slight departure from the vertical will not be serious, but for more accurate measurements it is clear that the coil system must be wound on an accurately turned cylinder which can be adjusted with its axis vertical.

§ 5. EXAMINATION OF ERRORS

The exact current necessary for the compensation of the vertical field may be found in two ways, either by successive adjustment until no deflection occurs on reversal of the solenoid current, or by interpolation from the deflections produced on reversal when the current in the coils is a little too small or a little too large. The first method was found to be much the easier and the more satisfactory, although, in the tests made, both gave identical results within the limits of experimental error. The first method was therefore always employed.

In the following experiments the procedure usually adopted was for one observer to record the deflection produced on reversal of the solenoid current. A second observer adjusted the current in the coils until the first observer signalled that exact compensation was attained. The compensating current was then read. Two observers are not necessary, but in these tests they made for more speedy progress.

To investigate the presence of errors of the type described in the first portion of the last section, as well as any due to the heating of the suspension, the magnitude of the solenoid current was varied. The tests were confined to currents which produced a fairly high degree of magnetization of the mu-metal. For cylinder no. 1 the successive values obtained for the compensating current with a current of 12 mA. through the solenoid were 79·7, 79·9, 79·9 and 79·65, giving a mean value of 79·79 divisions on the shunted millivoltmeter. With a current of 30 mA. through the solenoid, and other experimental arrangements unchanged, the successive values were 79·8, 79·9, 79·8 and 79·7, giving a mean value of 79·80 divisions. There was, then, no change with the higher current, and since the corresponding scale deflections were larger with the higher current, it was usually employed with cylinders wound like no. 1. Heavier currents caused appreciable sagging of the suspension owing to expansion, and produced frequent changes of zero due to convection currents; they were therefore not employed.

The errors due to the presence of the horizontal component of the earth's field were next investigated; these should be very small if the cylinder is properly mounted. With the system on which the last tests were made, and a current of 30 mA. through the solenoid, the following values of the compensating current were obtained: 79·5, 79·4 and 79·5 divisions. The apparatus was then turned through 180° in a horizontal plane and the following readings were obtained: 79·6, 79·65, 79·6, 79·75 and 79·55 divisions. It was then restored to its original position, and the following readings were recorded: 79·4, 79·6 and 79·55 divisions. The mean values for the two positions were therefore 79·49 and 79·63 respectively, so that the final error due to the horizontal component of the earth's field was certainly small. The value for the vertical component of the earth's field obtained from these determinations was 0·3931 gauss, a value consistent with the laboratory structure.

Tests were also made with cylinder no. 3. The sensitiveness of the apparatus with this cylinder was very high, a deflection of about 30 cm. being recorded on the reversal of a current of 12 mA. in the solenoid when no current flowed in the Helmholtz coils. It was now not necessary to use more than 12 mA., owing to the large number of windings in the solenoid.

With the apparatus in one suitable position the following values for the compensating current were obtained: 78·40, 78·35, 78·40, 78·30 and 78·30 divisions. The apparatus was then turned through 180° in a horizontal plane and the values now obtained were 78·50, 78·50, 78·55, 78·50, 78·50, 78·50, 78·35, 78·55 and 78·50 divisions. It was then replaced in its former position and the values obtained were 78·45, 78·45, 78·55, 78·55 and 78·55 divisions. The mean of all these values gave a value of 0·3926 gauss for the vertical component of the earth's field.

The first set of these readings gives a lower mean value than the last set. It should be recorded, however, that in the first set the zero error of the millivoltmeter was much larger than ever observed in any other set, probably due to a stray thermoelectric effect in the circuit. The first set may therefore be in error. If the mean of the second and third sets only is taken, the value of the vertical component obtained is 0·3929 gauss, which compares well with the earlier value of 0·3931 obtained with the first system. The three sets of readings show, however, that the cylinder system was well mounted.

In order to determine the magnitude of the error likely to arise through the line *AD*, about which the cylinder turns, failing to coincide with a horizontal line in the magnetic meridian, the apparatus was purposely inclined at various angles to the horizontal.

With cylinder no. 2, the levelling screw *L*, figure 3, was first screwed into the base to the maximum extent, so that the line *AD* made an angle of 1° 12′ with the horizontal. With the apparatus so placed that the screw *S* was to the north of the cylinder, the neutralization current was found to be 81·27 divisions. The apparatus was then turned through 180° when the neutralization current was 79·89. On restoring the apparatus to the first position the neutralization current was 81·31 divisions. The mean value for the two positions was therefore 80·59 divisions.

The suspension was then made as horizontal as possible, by sighting, and the currents with the screw *S* north and south of the cylinder were now respectively 79·88 and 81·25 divisions, the mean value being 80·57. It will be observed that the neutralization current for the first position had become the smaller.

The screw *L* was then unscrewed to the maximum extent, so that the line *AD* made an angle of 5° with the horizontal. The two neutralization currents were now 77·82 and 83·53 divisions respectively, giving a mean of 80·68. Hence, for a displacement of over 6° a difference of only one part in 800 between the mean values was produced.

This error may be made insignificant, for it is clear that for some setting of the apparatus the neutralization currents must be identical. In that event the line *AD* will be strictly horizontal if it lies in the magnetic meridian, which is practically the case.

In determining this setting a simple graphical method was found very effective. The screw *L* was screwed in as much as possible and a datum line was marked upon its head. The neutralization current was measured with the apparatus so placed that *L* was to the north of the cylinder. The screw was then turned through one complete turn and the neutralization current was again measured. This procedure was repeated several times. The apparatus was then turned through 180° and the measurements were repeated with *L* to the south of the cylinder. A set of results, obtained with cylinder no. 2, are plotted in figure 6. It will be seen that the best position of the apparatus was that obtained by turning the screw *L* through 3·2 turns from the zero position. This was done, and the values of the two currents were then found to be 80·10 and 80·18 divisions respectively, giving a mean of 80·14. The values of the vertical component of the earth's field calculated from the mean of the observations, from the graph of figure 6, and from the measurements with the best setting were respectively 0·3927, 0·3925 and 0·3928 gauss.

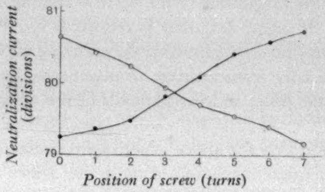


Figure 6. Cylinder no. 2.

Experiments on these lines were also made with cylinder no. 4, the current in the solenoid being 24 mA. Determinations of the neutralization currents were made for six recorded positions of the screw *L*. The value of the vertical component found from the mean of these six determinations was 0·3928, that found graphically was 0·3931, and, finally, that obtained from determinations when the apparatus was set in the most favourable position given by the graph was 0·3931 gauss. The corresponding graph was very similar to that of figure 6.

§6. COLLECTED RESULTS

The results of the measurements with the various cylinders are given in the table.

Specimen no.	Date of determination	V	Remarks
1	11. v. 32	0·3931	Zero error large
3	18. v. 32	0·3926	
2	27. v. 32	0·3939	
2	30. v. 32	0·3927	Direct mean
		0·3925	Value from graph
		0·3928	Best position
4	1. vi. 32	0·3928	Direct mean
		0·3931	Value from graph
		0·3931	Best position

The last two sets of results are considered to be the most accurate. However, even the earlier results show that it is possible, without taking any rigorous precautions, to determine the magnitude of the vertical component to within 1 part in 400 in a few minutes. If higher accuracy is required, the procedure described in the preceding section may be used, and then the accuracy appears to be limited only by the accuracy of the current-measuring arrangements, the surface of the table on which the brass frame rests, and the accuracy of the winding of the Helmholtz coils.

It should be recorded that the above experiments indicated that, provided care was taken to ensure adequate insulation of the wires drawn through the hole, the drilled cylinders such as nos. 3 and 4 were the most satisfactory. Moreover, the cylinders wound with no. 36 s.w.g. wire were much the easier to adjust and mount symmetrically, and they exhibited far fewer displacements of zero, which probably arise from slight changes in the positions of the thin ends of the solenoid.

There appears to be no reason why the apparatus, including the coil system, should not be designed in a portable form suitable for work in the field.

§7. DETERMINATION OF THE HORIZONTAL COMPONENT

It is clear from the diagrams of figure 3 that the apparatus may also be used for the determination of the horizontal component of the earth's magnetic field. This is important, for a value of this component can be conveniently obtained by an independent method, and hence the behaviour of the apparatus can be checked. From figure 3 it will be seen that it is necessary to turn the whole apparatus through 90° in a vertical plane. The Helmholtz coils are now, of course, set with their axis parallel to the magnetic meridian. The axis about which the cylinder rotates is made vertical by means of the levelling screws H_1 and H_2.

The sources of error associated with the measurement of the horizontal component are essentially those described in the earlier portion of this paper. The chief error is due to the effect of the vertical component of the earth's field on the mu-metal cylinder when the axis about which the latter rotates is not strictly vertical. A slight displacement of this axis from the meridian is relatively unimportant, but its displacement from the vertical in the meridian gives rise to serious error. In the latter case, if the axis of rotation makes a small angle α with the vertical, the vertical component of the earth's field can be resolved into components, $V \cos \alpha$ and $V \sin \alpha$, respectively parallel and perpendicular to the axis of rotation. The latter component will produce a couple approximately equal to $V \sin \alpha . Ial$. If α is of the order of 1°, this couple is approximately equal to $0{\cdot}009\, Ial$.

This source of error may be eliminated by determining the neutralization currents with the apparatus in two positions differing by 180° in a horizontal plane, the mean value of these two currents being equal to the correct neutralization current. The most favourable position for the apparatus may be found by the method outlined in an earlier section.

For this, it is expedient to place the apparatus with the axis of the cylinder at right angles to the magnetic meridian and parallel to the line joining the screws H_1. The centre of the cylinder coincides with the centre of the coil system. The suspension is rendered as vertical as possible by adjustment of the screws H_1 and H_2, the suspension being sighted against two plumb-lines during the last operation; if the solenoid is well constructed this means that the axis of rotation is practically vertical.

Let us suppose that in this position the mirror faces north. A datum mark is made on the head of the screw H_2, which may then be turned through a series of known angles and the corresponding neutralization currents may be determined. The apparatus is now turned through 180° in a horizontal plane, so that the mirror faces south, and the neutralization currents determined for the same series of positions of the screw H_2. A set of such determinations is reproduced in figure 7*a*, cylinder no. 4 being used in this case because of its symmetry; the current in the solenoid was 24 mA. We see that the best position of the apparatus is obtained by turning the screw through two complete turns from the zero position of the table. This was actually the position in which the apparatus was initially placed by sighting with the aid of the plumb-lines. The correct neutralization current obtained from the graph was 35·90, and from the mean of the observations, 35·89 divisions. The value found from a series of observations specially taken with the apparatus in the best position was 35·90 divisions. The mean value of the horizontal component thus found was 0·1755 gauss.

Figure 7*a* effectively illustrates the appreciable difference between the two values of the neutralization current for the two 180° positions of the apparatus, when the axis of rotation is tilted in a north-south plane. On theoretical grounds the effect of an inclination in the east-west plane should be much less. Such inclinations were produced by turning the head of one of the screws H_1 through known angles; a set of observations so obtained with cylinder no. 4 is reproduced in figure 7*b*. The mean value of the neutralization current obtained from the graph of figure 7*b* is 35·93 and from the mean of the observations 35·98 divisions; the agreement is satisfactory. It will of course be recognized that the table on which the apparatus shown in figure 3 is placed must be levelled as accurately as possible.

The above determinations were checked by an entirely independent method. The apparatus shown in figure 3 was removed, and between the coils was placed a magnet and mirror system suspended by a very fine silk fibre. The neutralization current was now determined by a method described elsewhere*. The dimensions of the magnet were very nearly the same as those of the mu-metal cylinder, so that the neutralization conditions should have been the same in both experiments, except that for the check determination the coils had to be rotated slightly. The corrected mean value obtained for the neutralization current for several displacements of the coils was 35·94 divisions; the check is satisfactory.

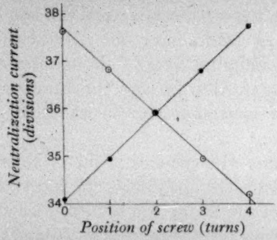


Figure 7*a*. Cylinder no. 4, north-south displacement.

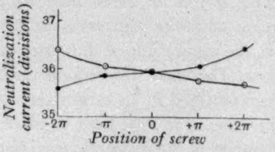


Figure 7*b*. Cylinder no. 4, east-west displacement.

If the axis of the Helmholtz coil system is not accurately horizontal and in the magnetic meridian, the experimental value of the neutralization current will be too high. Hence in an arrangement designed for very accurate determinations, both the coil system and the apparatus of figure 3 should be mounted on turntables. The coil table could then be placed in known positions and the position giving a minimum value of the neutralization current determined by a simple graphical method.

§ 8. ACKNOWLEDGMENTS

I again have very much pleasure in thanking Prof. E. N. da C. Andrade for his keen interest and support. I also wish to record my thanks to Mr A. Maxwell Lewis for his assistance in many series of test measurements.

---

* L. F. Bates, *loc. cit.*

DISCUSSION

Mr R. S. Whipple. Has the author considered the application of an instrument of this type to geophysical surveying? A higher degree of accuracy than the figures given in the paper would be necessary, but not improbably, with care in construction, this could be obtained. It would then be possible to use the same instrument in the field for the determination of the horizontal and vertical forces. Members might be interested to know that a Dye magnetometer has recently been constructed in which the Helmholtz coils are wound on metal formers, instead of on a marble cylinder as in the original instrument. In this way a portable instrument of high accuracy has been produced.

Mr Guild suggested that, as a null method was employed, the magnetizing solenoid need not be part of the suspended system. With a fixed solenoid, a small piece of mu-metal could be used in the suspension.

Author's reply. In reply to Mr Whipple: I see no reason why the instrument should not be made with greater sensitivity than I have so far employed, in a portable form suitable for geophysical surveying; in fact, I think it could be made very compact indeed.

In connection with Mr Guild's suggestion, I would like to point out that the difficulties of construction would be very considerably increased in providing fixed solenoids to magnetize the mu-metal, and I think additional sources of error would arise. In any case, the clamping of the moving system would be much more difficult.

547·532 + 547·551·1]: 536.63

A METHOD FOR THE DETERMINATION OF THE SPECIFIC HEATS OF LIQUIDS, AND A DETERMINATION OF THE SPECIFIC HEATS OF ANILINE AND BENZENE OVER THE APPROXIMATE RANGE 20° C. TO 50° C.

By ALLAN FERGUSON, M.A., D.Sc.
AND
J. T. MILLER, B.Sc., East London College

Received November 18, 1932. *Read December* 16, 1932.

ABSTRACT. The specific heats of aniline and benzene are determined by measuring the electrical power E^2/R necessary to hold the temperature of a calorimeter and its contents steady at various temperature-excesses θ. A cooling curve is then taken in order to evaluate the constant K in the equation

$$(MS + W) K\theta^{\frac{5}{4}} = E^2/RJ,$$

where S is the specific heat of the liquid at a temperature θ above that of the surroundings.

The specific heat of aniline at any temperature T between 20° C. and 50° C. is given by

$$S = \cdot 495_0 + \cdot 000275\,(T - 20) + \cdot 0000035\,(T - 20)^2,$$

and that of benzene by

$$S = \cdot 395_8 + \cdot 00125\,(T - 20).$$

§1. INTRODUCTION

There exists an increasing need for fairly precise values of certain thermal constants of organic liquids and solutions, which play an important part in technological processes—we refer especially to specific heats, specific volumes and latent heats. In this communication we confine ourselves to a measurement of specific heat and its temperature-variation over a moderate range.

A glance at the relevant entries in the standard books of tables shows that the figures quoted in them must be of very doubtful value*, so that it becomes necessary to consult the actual papers, and to assess for oneself the reliability of the final figures. We may say here that, in comparing our figures with those of other experimenters, we have retained only the results of Messrs Williams and Daniels† for benzene, which were obtained by the use of an adiabatic calorimeter, and of Dr H. R. Lang‡, who used the continuous flow method, for aniline.

We believe that there is room, and need, for an experimental method which can be used in precision work and yet, in a simple form, give with such ordinary apparatus as is to be found in every reasonably equipped works laboratory, results that can be depended upon to 1 per cent or better.

---

* For instance, Landolt and Börnstein give for the specific heat of aniline, 0·510, 0·499, 0·491 at 20° C. and for the specific heat of benzene, 0·4502, 0·441, and 0·438 at 50° C.

† *J. Amer. Chem. Soc.* **46**, 903 (1924).

‡ *Proc. R. S.* A **118**, 138 (1928).

The method to be described does, we think, approximate to these requirements, and when it is used under the conditions we indicate the results may be depended upon, as far as the physical work is concerned, to at least 1 part in 500, which was the standard we set ourselves at the outset.

Experience of the method has convinced us that, with standardization of corresponding accuracy, we may obtain results accurate to 1 part in 1000. Our results are certainly reproducible to about that order with the present apparatus.

§ 2. METHOD

In brief, the method consists in supplying by means of a heating coil, and measuring, the power necessary to hold a copper calorimeter and its contents at temperatures, for example, 5° C., 10° C., 15° C. ... higher than that of the surrounding medium, which is usually kept at about room-temperature. After the calorimeter and its contents have been raised to a temperature of about 50° C. the power is switched off, and a cooling curve is taken. This completes the experimental observations.

Then at any temperature θ° above that of the surroundings, if the power required to hold the temperature stationary is E^2/R watts, we have *E*, *R*

$$-\frac{dQ}{dt} = -(MS+W)\frac{d\theta}{dt} = \frac{E^2}{JR} \qquad \ldots\ldots(1),$$

where J has the value 4·186 or 4·1845, according as a watt is defined as 10^7 ergs per second or in terms of the international ampère. In our case the appropriate value is 4·1845, although to the order of accuracy contemplated in these experiments the difference between the two values is without numerical significance.

$-dQ/dt$ in the above equation represents the rate of loss of heat from the calorimeter and contents, M the mass of liquid contained in the calorimeter whose water-equivalent is W, and S the specific heat of the liquid at the given temperature. *Q*, *t* *M* *W*, *S*

If, now, we can show that

$$-\frac{d\theta}{dt} = K\theta^n,$$

and can determine the values of K and n, we have *K*, *n*

$$(MS+W)\,K\theta^n = E^2/RJ \qquad \ldots\ldots(2)$$

as the equation which gives the specific heat S at a temperature θ° above that of the surroundings*. For each value of E^2/R we can work out a value of S at the corresponding temperature. The unit in which S is measured is the 15° C. calorie. *S*

---

* It is the fact that we are enabled to express $-d\theta/dt$ as a simple function of θ which gives the method its power. But it must not be assumed that we claim any generality for the five-fourths-power law. We say no more than that it holds with very considerable exactness for the liquids which we have tested over the range 20° to 50° C. It may be necessary to search for a function of another form in other tests. The value of K with our particular calorimeter varies, of course, with the nature of the liquid in the calorimeter.

§ 3. EXPERIMENTAL ARRANGEMENTS

The simple arrangement adopted is shown in figure 1, which is almost self-explanatory. The copper calorimeter *A*, which is supported as shown, is 14 cm. from the base to the flange, has an internal diameter of 10 cm. and is about 0·45 mm. thick. The width of the flange is about 1·25 cm. The lid *B*, to which is attached the coil *C* with its current leads *D* and potential leads *E* and the stirrer *F*, is screwed down to the flange during the course of an experiment, a thin film of grease being placed on the flange beforehand. *G* is a casing containing the ball bearings for the stirrer. The thermometer is inserted at *H*.

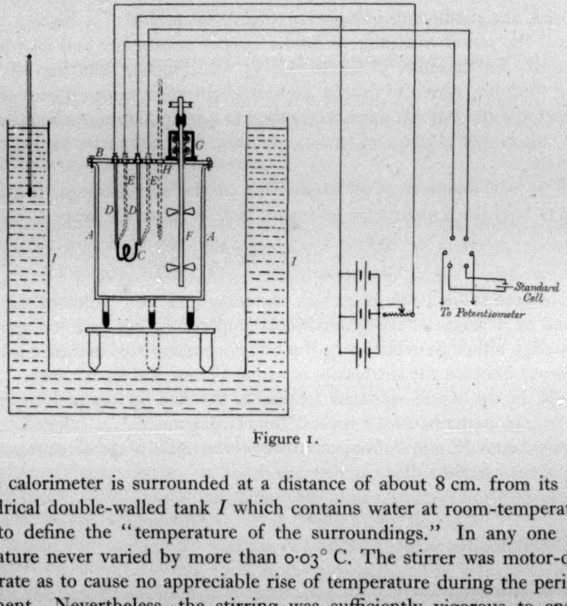


Figure 1.

The calorimeter is surrounded at a distance of about 8 cm. from its walls by a cylindrical double-walled tank *I* which contains water at room-temperature and serves to define the "temperature of the surroundings." In any one run this temperature never varied by more than 0·03° C. The stirrer was motor-driven at such a rate as to cause no appreciable rise of temperature during the period of an experiment. Nevertheless, the stirring was sufficiently vigorous to ensure appreciable uniformity of temperature throughout the mass of liquid. This was tested by systematically exploring the liquid by means of a sensitive thermocouple. Whatever the relative positions of the junctions, no difference of temperature so great as 0·1° C. could be detected at any stage of the heating.

At one stage of the proceedings, it was deemed that an exact knowledge of the temperature of the radiating surface of the calorimeter would be necessary, and experiments were made to test the temperature-gradient through the calorimeter walls by soldering thermo-junctions inside and outside. It was found that a slight difference of temperature was established which increased with the temperature-excess of the contents of the calorimeter as shown in table 1.

Table 1

Temperature-excess (° C.)	2·90	9·27	12·86	18·43	22·87	29·61
Temperature-difference (° C.)	0·00016	0·00019	0·00021	0·00024	0·00029	0·00031

The thermometer used for reading the temperature of the liquid in the calorimeter was graduated in tenths from − 5° to 50° C. with an auxiliary scale at 100° C. It was an excellent instrument, supplied by B. Black and Son. It was standardized by comparison with a first-grade thermometer possessing a N.P.L. certificate.

The coil was of eureka wire and had a resistance of 0·1101 Ω. Its resistance was determined by comparison with a standard half-ohm coil. The temperature-variation of its resistance was neglected.

The potentiometer used was a simple Gambrell instrument and was calibrated in the ordinary way. Both the resistance-comparisons and the measurement of the potential difference at the terminals of the heating-coil were made on this potentiometer, which was standardized by means of a Weston cell.

Current was supplied to the heating-coil from a battery of secondary cells of capacity 50 ampère-hours, arranged in three rows in parallel, with two cells in series in each row.

§4. THE NATURE OF THE COOLING CURVE

It may be well to mention here that, although it is usually considered unwise to read temperatures on a falling thermometer, we have nevertheless found no difficulty in obtaining a very smooth experimental curve, and in reproducing our results to a high order of accuracy. This is probably to be attributed to the slight but continuous shaking produced by the stirring.

A typical curve is shown in figure 2 and is designated curve A. The ordinate scale for this is shown under A on the y axis.

As is well known, the rate of heat-loss ($-dQ/dt$) from a vertical wall, cooling under clearly defined conditions by natural convection, is proportional to the five-fourths ($\frac{5}{4}$) power of the temperature-excess. In this experiment, the calorimeter is losing heat very slightly by conduction, very slightly by radiation (this loss being minimized by highly polishing the external surface) and mainly by convection. We find, however, purely empirically, that the *rate of fall of temperature* ($-d\theta/dt$), and *not* the rate of heat-loss, is connected with the temperature-excess θ by the equation

$$-d\theta/dt = K\theta^{\frac{5}{4}} \qquad \text{......(3).}$$

Whatever the régime, equation (1) holds at any stage of the cooling; and combining this with (3) we have, *under the conditions of cooling just specified*,

$$(MS + W)\,K\theta^{\frac{5}{4}} = E^2/RJ \qquad \ldots\ldots(4)$$

as the equation from which to determine the specific heat S at any temperature-excess θ.

We have now to consider how we establish the validity of (3). This leads by integration to

$$\theta^{-\frac{1}{4}} - \theta_0^{-\frac{1}{4}} = \tfrac{1}{4}Kt \qquad \ldots\ldots(5),$$

where θ_0 is the initial temperature-excess corresponding to the zero value of t. Experiment has furnished us with a series of values of θ and t. Hence if we plot

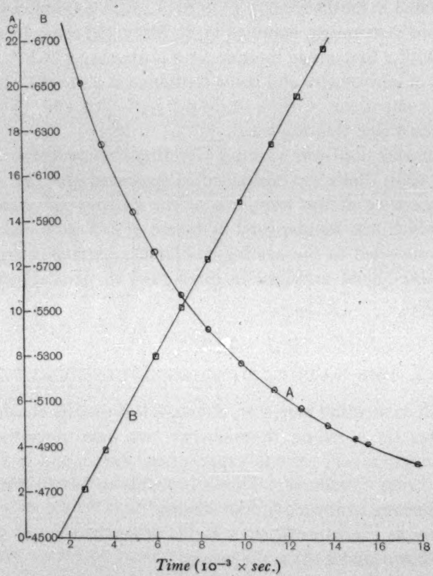


Figure 2. Ordinates of curve A are ° C., ordinates of curve B are $\theta^{-\frac{1}{4}}$.

$\theta^{-\frac{1}{4}}$ against t we obtain, if (3) holds, a straight line, the slope of which determines K. Such a line is the line B in figure 2; its ordinate scale is to be found under B on the y axis.

K may also be determined by a simple application of the rule of least squares to (5), and, in practice, we employ both methods. The graphical method, however, serves to test the equation as well as to determine K. It has been suggested that, in the very moderate temperature-range with which we are concerned, the form of the law employed is a matter of secondary importance. It would not be difficult to devise a method by which, without assuming the $\frac{5}{4}$-power law, equation (3) might be tested by putting n for $\frac{5}{4}$ and determining its value experimentally. But we have thought it sufficient to assume the quasi-Newtonian form $-d\theta/dt = K\theta$ and to make a plot of log θ against t, using our experimental data. The resulting line shows appreciable curvature, and indicates that the Newtonian law is certainly not applicable. The agreement between the observed and calculated values of θ using the $\frac{5}{4}$-law is shown for an experiment with aniline in table 2.

Table 2

t (sec.)	θ observed (° C.)	θ calculated from K_1 (° C.)	θ calculated from K_2 (° C.)
0	30·69	—	—
2700	20·15	20·11	20·14
3660	17·44	17·49	17·46
4500	15·48	15·53	15·51
6000	12·68	12·69	12·67
7200	10·76	10·84	10·82
8460	9·23	9·28	9·26
9900	7·77	7·81	7·80
11400	6·59	6·57	6·56
12600	5·75	5·76	5·75
13800	5·07	5·07	5·06
15000	4·49	4·48	4·47
15600	4·21	4·22	4·21
17800	3·36	3·38	3·37
18300	3·19	3·22	3·22
19500	2·88	2·89	2·89
22000	2·33	2·32	2·32

[K_1 found graphically $= \cdot 07004 \times 10^{-3}$; K_2 calculated by the method of least squares $= \cdot 07012 \times 10^{-3}$.]

§5. THE WATER-EQUIVALENT OF THE CALORIMETER

The water-equivalent of the calorimeter was determined by filling the calorimeter with water, and performing an experiment similar to that described. The experiment provides a fairly stringent test of the method, inasmuch as the water-equivalent is but about 12 per cent of the water-equivalent of the whole mass.

After carrying out the experiment as indicated, and using the equation

$$(MS_w + W)\,K\theta^{\frac{5}{4}} = E^2/JR,$$

we found that the water-equivalent increased linearly with the temperature. The *International-Critical-Tables* values of the specific heat of water S_w at the respective temperatures were used for calculating the results. S_w

The relation between W and T can be expressed by

$$W_T = W_0\,(1 + \cdot 0005541),$$

where T is Centigrade temperature on the thermodynamic scale.

The agreement between the observed and calculated values of W is shown in table 3.

Table 3

Temperature T	22·05	26·33	33·31	38·32	40·65	45·25
W observed	71·22	71·39	71·67	71·87	71·99	72·21
W calculated	71·16	71·29	71·61	71·86	71·93	72·05

δ The calorimeter is almost completely of copper. δ, the specific heat of copper, is given very closely by the following relation*

$$\delta = \cdot 09088\,(1 + \cdot 0005341\,T - \cdot 00000048\,T^2)$$

between 0° C. and 100° C.

It will be seen that, although the water-equivalent of the calorimeter is but a small fraction of the whole water-equivalent, the method is sensitive enough not only to determine its value, but also to indicate fairly closely the magnitude of the temperature coefficient.

The water-equivalents used in subsequent calculations are, of course, those appropriate to the temperatures concerned.

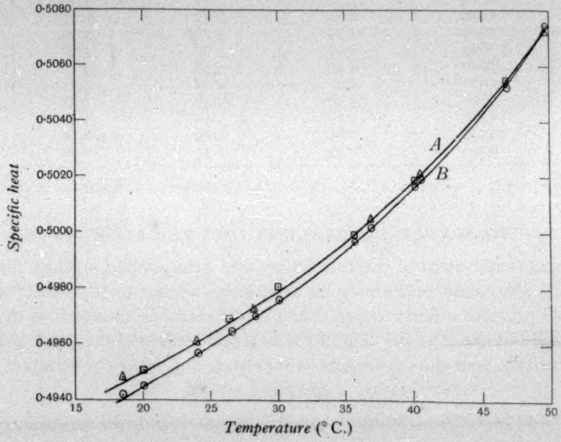


Figure 3.† Aniline: Ferguson and Miller's results, A; Lang's results, B.

---

* E. H. Griffiths and E. Griffiths, *Phil. Trans.* **213**, 119 (1914). *Proc. R. S.* **88**, 549 (1913); **90**, 557 (1914).

† Amended: see the discussion, p. 207.

§6. RESULTS FOR ANILINE

Although aniline has been widely used as a test liquid, it is by no means an ideal liquid on which to test a new method; it is hygroscopic and it polymerizes. The aniline used was of research quality and was dried over calcium chloride. It was then distilled and was collected in a closed flask which had previously been cleansed and dried by passing warm dry air through it for a considerable period. The calorimeter after being polished was similarly treated, and the aniline was transferred to the calorimeter by a siphoning process which involved practically no contact with undried air, the air which entered the storage flask as the aniline escaped being drawn over calcium chloride. The experiment was carried out as described, with the results as tabulated below in table 4. In this and other tables, T stands for Centigrade temperature, and θ for the temperature excess.

Table 4

(*a*) *Heating experiment*

Mass of liquid = 1099·30 gm.

E^2/R (W.)	Temperature of surroundings (° C.)	Temperature of calorimeter (° C.)	Temperature-excess (° C.)	Water-equivalent W	Specific heat S
0·6688	17·18	20·08	2·90	71·16	0·4951
2·8687	17·18	26·45	9·27	71·47	0·4969
4·3278	17·19	30·05	12·86	71·55	0·4981
6·8024	17·20	35·63	18·43	71·67	0·5000
8·9541	17·20	40·07	22·87	71·97	0·5019
12·4512	17·21	46·82	29·61	72·29	0·5054

[K_1 found graphically = $0{\cdot}07004 \times 10^{-3}$; K_2 found by the method of least squares = $0{\cdot}07012 \times 10^{-3}$.]

(*b*) *Cooling experiment*

Temperature of calorimeter (° C.)	Temperature of surroundings (° C.)	Time t (sec.)	Temperature of calorimeter (° C.)	Temperature of surroundings (° C.)	Time t (sec.)
47·90	17·21	0	22·95	17·20	12600
37·36	17·21	2700	22·27	17·20	13800
34·65	17·21	3660	21·69	17·20	15000
32·69	17·21	4500	21·41	17·20	15600
29·89	17·21	6000	20·54	17·19	17800
27·97	17·21	7200	20·38	17·19	18300
26·43	17·20	8460	20·07	17·19	19500
24·97	17·20	9900	19·52	17·19	22000
23·79	17·20	11400			

A second experiment gave almost identical figures for S, and these together with the values found by Dr Lang are shown in table 5 below.*

---

* In his paper Dr Lang's results are given in terms of the 20° C. calorie. In table 5, however, the values have been recalculated in terms of the 15° C. calorie. See the discussion, p. 207.

Table 5

Experiment 1

T	20·08	26·45	30·05	35·63	40·07	46·82
S (F. and M.)	0·4950	0·4969	0·4981	0·4999	0·5019	0·5054
S (H. R. L.)	0·4945	0·4965	0·4976	0·4997	0·5017	0·5052

Experiment 2

T	18·45	24·06	28·24	36·96	40·59	49·62
S (F. and M.)	0·4947	0·4961	0·4972	0·5005	0·5019	0·5073
S (H. R. L.)	0·4943	0·4957	0·4971	0·5003	0·5020	0·5074

Our results are very satisfactorily represented by the equation

$$S = 0{\cdot}495_0 + 0{\cdot}000275\,(T - 20) + 0{\cdot}0000035\,(T - 20)^2$$

and agree with those of Dr Lang to about 1 part in 1000. The results are shown graphically in curve A of figure 3, where the □'s and △'s represent our values for experiments 1 and 2 and the circles represent Dr Lang's values, the curve for these being designated B.

The values of the specific heat of aniline calculated from the formula just given are compared with the observed values in table 5*a*.

Table 5*a*

T	S observed	S from formula
20·08	0·4951	0·4950
26·45	0·4969	0·4969
30·05	0·4981	0·4982
35·63	0·5000	0·5002
40·07	0·5019	0·5021
46·82	0·5054	0·5053

§7. RESULTS FOR BENZENE

The benzene used was guaranteed free from thiophene or sulphur and was tested for freedom from thiophene by the fact that isatin dissolved in sulphuric acid showed no blue coloration when shaken with the benzene. Freedom from sulphur was indicated by the fact that no discoloration of mercury took place when the benzene had been shaken with concentrated sulphuric acid.

The benzene was fractionally crystallized, the portion employed in our experiments melting at 5·48° C. It was transferred to the calorimeter, with precautions similar to those just detailed, and the experiment was carried out in the manner described. The results of two independent runs are given in table 6, and the values obtained by Williams and Daniels are appended for comparison.

Although not overtly stated, it may be inferred from Williams and Daniels' paper that the results are in terms of the 20° C. calorie. The results obtained by these two experimenters are shown in curve *B*, and our results on curve *A* of figure 4.

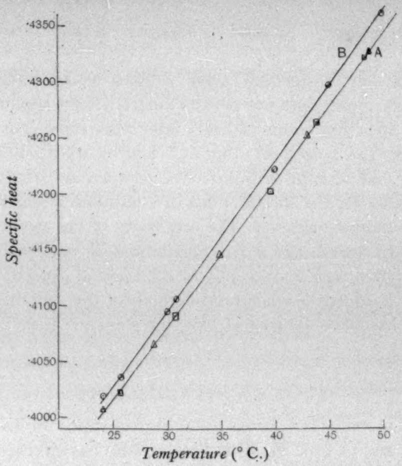


Figure 4. Ferguson and Miller's results, *A*; Williams and Daniels' results, *B*.

Table 6

Experiment 1

T	22·61	25·62	30·69	39·51	43·93	48·56
S (F. and M.)	0·3993	0·4025	0·4092	0·4220	0·4264	0·4321
S (W. and D.)	0·4015	0·4044	0·4106	0·4236	0·4280	0·4336

Experiment 2

T	24·03	28·65	34·80	42·83	48·89
S (F. and M.)	0·4008	0·4066	0·4147	0·4252	0·4325
S (W. and D.)	0·4022	0·4081	0·4162	0·4278	0·4340

The results, which on the average differ from those of Williams and Daniels by about 1 part in 500, are very fairly represented by the equation

$$S = 0{\cdot}395_8 + 0{\cdot}00125\,(T - 20).$$

The values of the specific heat of benzene calculated from the formula just given are compared with the observed values in table 6*a*.

Table 6*a*

T	22·61	25·62	30·69	39·51	43·93	48·56
S observed	0·3993	0·4025	0·4092	0·4220	0·4264	0·4321
S calculated	0·3995	0·4026	0·4093	0·4221	0·4265	0·4322

It would seem that the method is not without its advantages. It is easy in application, is fairly rapid, does not demand any excessive quantity of liquid, and may, with simple apparatus of the ordinary laboratory type, give results which are of accuracy greater than 1 per cent. Our own figures, we think, may be depended on to 1 part in 500 and we hope to improve the accuracy and range of our apparatus so as to obtain values for the specific heats of a number of important liquids over the range of their normal existence. The sensitivity of the method is considerably greater than we had hoped, and it has possibilities as one for determining, with precision, the variation with temperature of the thermal capacity per unit mass of water*. At least, it affords a laboratory method for the determination of Joule's equivalent which has some advantages over the standard electrical method of the text-books.

§8. ACKNOWLEDGMENTS

It is a pleasure to record our thanks to Dr Ezer Griffiths for his advice on certain technical matters, and to Prof. H. R. Robinson, who has afforded us every facility for the carrying out of the experiments.

DISCUSSION

Dr H. R. Lang. The authors have developed a simple calorimetric method that promises to give accurate results without difficulty. It is certainly a little disturbing to find that the usual elaborate precautions which are deemed necessary in calorimetric work of precision seem to have been omitted without any consequent appreciable decrease in accuracy. I am a little uncertain, however, about the efficiency of the stirring, and suggest that the authors should determine the temperature-gradient between the outside wall of the calorimeter and the centre of the liquid.

The comparison of results expressed in different units is surely not quite just. One does not think of comparing lengths in centimetres and inches; it is not so very different, I venture to suggest, to compare measurements in different calories.

---

* We have carried out some preliminary experiments to test this point, and have obtained values for the specific heat of water, over the range 20° to 50° C., in very close agreement with those obtained by Callendar and Barnes. We hope to extend the range of these observations in the near future.

I would therefore urge the authors to make the simple conversion, and to amend the tables and graphs before the paper is published in the *Proceedings*. It happens that the difference between the two calories accounts almost exactly for the divergence between the authors' results and those of other observers. The authors have omitted to include the units of specific heat in their tables. This, I assume, is an oversight.

Could the authors make a determination of the freezing-point of a sample of their aniline after an experiment? This would give a figure for the water content, and dispense with any assumption about its magnitude. I should be particularly grateful if the authors would make some measurements on aniline below 5° C. where my results were consistently peculiar.

Finally, may I suggest to the authors, that in view of some experiments that my colleagues and I have carried out during the past few years, when they make their experiments with water above 50° C. they should take the greatest care to ensure that it is quite air-free and that no air can dissolve in it during the experiment.

Dr Ezer Griffiths. This is an interesting development of the technique of the cooling-curve method of measuring specific heats of liquids. The authors have not referred to one useful feature of their method, namely that a single calibration will suffice for a series of different liquids, so that the method simplifies the problem of the heating-coil when corrosive fluids are dealt with.

As regards the calorie to be adopted the position is as follows:

A meeting of the International Union of Physics was held in Brussels in 1931. At this meeting discussion took place on matters brought forward by national committees. The British National Committee, represented by Sir Richard Glazebrook and myself, submitted a proposal as to the definition of the calorie. As a result of the discussion on this and other proposals a sub-committee was appointed to deal with symbols, units, and nomenclature in physics and to report to the General Assembly. At the first meeting of this sub-committee, Prof. Kennelly being in the chair, the following resolution was agreed to unanimously:

That this Commission recommends to the Executive Committee of the International Union of Physics that the following two propositions be communicated to the next General Assembly as recommendations from this Commission:

(1) That the unit of heat when measured in units of energy be the Joule, defined as equivalent to 10^7 ergs.

(2) That the gramme-calorie be the amount of heat required to raise the temperature of one gramme of water from 14·5° to 15·5° of the international scale of temperature.

Dr J. H. Brinkworth. I should like to ask whether the truth of the empirical law $d\theta/dt = K\theta^{\frac{5}{4}}$ was established for liquids having large temperature coefficients of specific heat. It seems that heat-losses of all kinds are effective in establishing this law, but the experimental conditions must be identical both during the stationary-balance experiment and during the cooling. If during the latter the current used in the former is sent through one pair of potential and current leads, the conditions will be the same.

Mr J. H. Awbery. Of the various calorimetric methods which have been suggested, the one in which the temperature of a surface is used as a measure of the heat-flow from it, by means of a special calibration, has been perhaps the least employed. Prof. Lees used it about 36 years ago for conductivity-measurements, but he did not regard it as very accurate. To apply this method to specific-heat work is even more difficult, because in this case the flow is not steady. The authors therefore made a great advance when in one step they overcame this difficulty, and made the method a precise one. This they did by the device of fitting a curve of defined mathematical form to the cooling or heating curve. In this connexion, may I ask the authors whether, in addition to proving that $d\theta/dt = K\theta^{\frac{5}{4}}$, they also proved that $-dQ/dt = K'\theta^{\frac{5}{4}}$? It seems to me that, within experimental error, both might be true.

A second point to which I would refer is in table 1. It was valiant of the authors to try to measure such small temperature-differences, but surely the results only prove that the fall in temperature through the copper is negligible? Actually, each line of the table is a measure of the heat-flow and they hardly seem to bear out the $\theta^{\frac{5}{4}}$ power law. One quantity changes twofold when the other changes tenfold.

The suggestion of using the method to study the heat-capacity of water is a very attractive one, and I doubt not that I shall be like many others in looking forward to the results.

Mr J. H. Coste. The method described is interesting as yielding the specific heat at a defined temperature, rather than, as is usually the case, over a small range of temperature. It is not quite clear from the description of figure 1 how much of the adjuncts of the calorimeter vessel are included in the water equivalent, or of what material the lid, for instance, is made; but as the calculated and observed values agreed so well the question is one of interest rather than importance.

By their opening reference to organic liquids which play an important part in technological processes the authors may be considered to justify the statement that the method does not require any excessive quantity of liquid, but the volume used seems to have been rather more than a litre, which in many cases of only scientific interest would be a large amount to prepare. The value of the data for aniline would be more securely established if it could be stated that the dry liquid boiled within certain limits, or if other more precise criteria than the statement that it was of "research quality" could be given.

For an experiment where much depended on the temperature of the surroundings the means used to define this seem rather crude, as the thermometer shown in figure 1 only gives the temperature of the unstirred water in its vicinity, whereas the relevant temperature is that of the inner surface of the tank. Probably the mass of water in the jacket was very large and the room temperature very constant, but a statement to this effect would be useful. The method appears to be capable of considerable precision and to be convenient. It would be of interest if the authors would use it to determine the specific heats of other pure organic liquids.

AUTHORS' reply. We desire to thank those who have contributed to the discussion for their very helpful comments. To the order of accuracy contemplated, we found the temperature-gradient to be negligible between all the very widely distributed points selected. We have adjusted the results obtained by different experimenters so that in the corrected pages all results are expressed in terms of the same calorie; but in the matter of specific-heat units we are proof against Dr Lang's wiles, and refuse to be drawn into a discussion on that point. Dr Ezer Griffiths' remarks show very clearly the relations between the units involved. We shall bear in mind his suggestions in an extended series of observations which we may undertake.

In reply to Dr Brinkworth's remarks: The empirical law assumed has been tested for the liquids specified in the paper. It may happen that, with other liquids, a different form of $f(\theta)$ must be assumed, but this will in no way invalidate the principle of the method. As Dr Brinkworth points out, the conditions in the "statical" and "dynamical" experiments must be identical. In experiments with different liquids K varies, of course, from liquid to liquid, even if the five-fourths-power law holds.

No; we did not attempt to test whether $-dQ/dt = K'\theta^{\frac{5}{4}}$. We propose to make a study of the rate of heat-loss a separate problem. We thank Mr Awbery for his kindly description of our attempt to find the temperature-gradient through the cylinder as "valiant." Remembering a well-known line of Pope, we might well choose another epithet to describe our effort. As Mr Awbery quite correctly remarks, it simply shows that the temperature-drop through the copper is negligible.

We thought that the method of determining the water equivalent showed clearly enough how much of the calorimeter and its adjuncts entered into the water equivalent. The material of the calorimeter was practically all copper, save for a brass flange to which the lid was attached. The liquids used were bought as of "research quality" and were dried, and fractionally distilled or crystallized in the ordinary way. As Mr Coste correctly surmises, the mass of water in the enclosing tank was very large, and, as the experiment was carried out in a secluded corner of the laboratory, constant temperature or, rather, *very* slowly varying temperature conditions were closely fulfilled.

We hope to carry out experiments over a wide range of temperature, using a great variety of pure liquids.

551·594·11

THE IONOSPHERE AS A DOUBLY-REFRACTING MEDIUM

BY PROF. E. V. APPLETON, F.R.S.

AND

GEOFFREY BUILDER, B.Sc.,
King's College, London

Received November 17, 1932. *Read December* 16, 1932.

ABSTRACT. In a previous communication to the Society the occurrence of wireless echo doublets was described and was provisionally attributed to the influence of the earth's magnetic field on the dispersive properties of the ionosphere. A more extended study of the subject, which has included an experimental determination of the polarizations of the doublet-components, has confirmed this hypothesis. In South-east England, for ionospheric reflection at vertical incidence, the echo-component of lesser delay is, in general, of right-handed, and the component of greater delay of left-handed, circular polarization, but this temporal sequence should be reversed in the Southern Hemisphere, and in certain special circumstances in the Northern Hemisphere.

§ 1. INTRODUCTORY

In the experimental study of the ionosphere* by electric wave reflection it is very frequently found that the reflected signal resulting from a single incident pulse consists of a doublet, the components of which are separated by a small time-interval. Appleton and Builder†, who described this phenomenon, suggested that it was possibly due to the influence of the earth's magnetic field, the two components being, in fact, the two elliptically polarized waves of opposite rotational sense into which the incident wave is split by magneto-ionic double refraction. Much further work has been since carried out on this subject, the result of which provides strong support for this interpretation. Such work forms the subject of the present communication.

§ 2. THE EXPERIMENTAL FACTS

The first curve given by Appleton and Builder, in which the equivalent height of the upper reflecting region was plotted as a function of time, showed that as the night advanced the temporal separation of the components of the echo gradually increased. Owing to electron-limitation, reflection eventually ceased to be marked, but it was found that the echo-component of greater delay was lost, owing to this cause, earlier during the night than was the echo of shorter delay. On the incidence of sunrise, however, the re-appearance of the echo of shorter delay was observed almost half an hour before the other appeared. This evidence suggested very strongly that a greater concentration of electrons is required to return the longer delay component than is required for the shorter delay component.

---

* This is a convenient term, suggested by Mr R. A. Watson Watt, to connote the whole of the ionized regions of the upper atmosphere.

† *Proc. Phys. Soc.* **44**, 76 (1932); see also Rukop and Wolf, *Z. f. Tech. Phys.* **13**, 132 (1932); and White, *Nature*, **129**, 579 (April 1932).

Various other experiments of the same kind have amply confirmed this interpretation, but perhaps another way of demonstrating the point is even more conclusive. One of the most useful indices of ionospheric conditions is a curve illustrating the relation between equivalent height of reflection and electric wave frequency. An example of such a curve is shown in figure 1. The data for it were obtained in the period 2353 G.m.t. on April 29 to 0020 G.m.t. on April 30, 1932, in experiments carried out between East London College and King's College, London. It will be seen that the phenomenon of splitting is more marked the higher the frequency, and that the F_1'' component penetrates the layer and is lost for a lower critical frequency than is the case for F_1'. The curve also suggests that even for the lower range of frequencies the phenomenon of splitting actually occurs, but, because of the small temporal separation, the components are not resolved. This point could perhaps be settled using signal pulses of very short duration indeed. It may, however, be mentioned that for conditions represented by, say, A in figure 1 the essentially double nature of the echo signal is often indicated by marked intensity-variations in the central part of the pulse, the variations of the beginning and end being by no means so marked. These variations of intensity are naturally explained as being due to interference between the two parts of the components which overlap in time, and the phase difference of which is gradually altering.

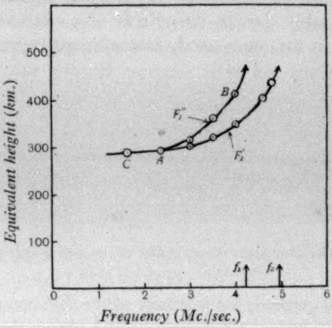


Figure 1. Curve illustrating relation between equivalent height and frequency. F_1' extraordinary; F_1'' ordinary ray.

Evidence derived from instances of multiple reflection also points very definitely to an interpretation in terms of the magneto-ionic theory. When the doubling of signals also occurs, the type of record obtained is that shown in figure 2 which is reproduced from our paper on wireless echoes of short delay. Here the received signal is shown as a function of time, the time scale being indicated by the lower trace of frequency 1115 cycles per second. The ground signal G is followed by the component echoes F_1' and F_1'' of the first order and later by the corresponding second order reflections F_2' and F_2''. Now the fact that F_1' and F_1'' on their return to the upper atmosphere are not split again indicates that their polarization must be different from that of the waves incident on the layer at the first reflection. That they are reflected without further doubling does, in fact, appear to indicate that their polarizations are those which travel without change within the ionized medium. Also the fact that the temporal interval $F_1'F_2'$ is less than the corresponding interval $F_1''F_2''$ for the other component shows that F_1' and F_1'' must be differently polarized. Observations on the relative intensities of the two echo-components made from a large number of records have enabled us to make the following statements. For conditions such as are indicated by B in figure 1 the component of greater delay is of lower amplitude than the component of lesser delay. This is presumably due to the effects of electron-limitation in causing impaired reflection. On the other hand, as conditions represented in point A in the same figure are approached, the intensity of the F_1'' component relative to F_1' increases and ultimately becomes the greater. This shows that the polarization for conditions represented by a point such as C is determined by the polarization of the stronger component F_1''. Now in some unpublished experiments carried out in 1930, using the frequency-change method of determining polarization, it was found that, for conditions in which splitting was not marked and for conditions such as may be represented by point C in figure 1, the polarization of 100-metre waves reflected from the upper region was approximately circular and left-handed*. The combined evidence therefore indicates that the polarization of F_1'' is left-handed and that of F_1' right-handed.

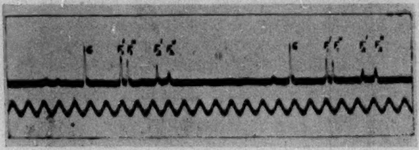


Figure 2. (The time scale shown under the record is that provided by an alternating current of 1115 ~.)

Although our early observations on echoes, made in the summer of 1931, showed the phenomenon of splitting in its simple form, the returned echo being in the form of a doublet, much more complicated results were obtained during the winter of 1931–2 to be followed again by simpler cases in the summer of 1932. An example record of one of the more complicated types of splitting is shown in figure 3. It represents a case of reflection from the upper region, and was obtained at 0226 G.m.t. on November 26, 1931, with a wave-length of 90 metres.

Although patterns of this type are sometimes so complicated as to be difficult to unravel, it is always clear that the first part of the returned signal fits exactly on the F_1' portion of the (P', f) curve*. This fact strongly suggests that the phenomenon is magneto-ionic in origin and that the first part of the complicated signal possesses normal characteristics and is therefore of right-handed polarization, the second and more complicated portion of the signal being associated with the left-handed component of greater delay. At the same time we may note that the more complicated type of splitting occurs only under conditions (e.g. winter and/or pre-dawn) when the ionization-gradient of the upper region is low. Further reference to this point is made below.

---

* The observer is here supposed to be looking in the direction of propagation.

In attempting to settle definitely the actual polarization of the two supposed magneto-ionic components, experiments were carried out with a new type of polarization analyser†. It will at once be seen that the problem of determining the polarization of two signal impulses which follow one another with a very short time-interval is quite different from that involved in previous polarization investigations in which cases the frequency-change method and a sustained signal have been employed. For our present purpose it is not sufficiently convenient to determine the resultant polarization of either the combined effect of ground waves and downcoming waves or even of the resultant polarization of the two components on a suppressed ground-wave receiving system. The more straightforward way is to determine separately the polarizations of ground wave and of the echoes as they successively occur in time. This demands an indicator of very rapid response, such as the cathode-ray oscillograph.

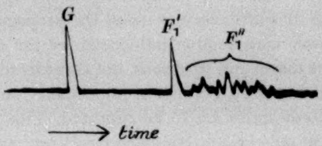


Figure 3.

In the new type of radio-polarimeter, which has been developed at Radio Research Station, Slough, two similar frame aerials are used at right angles and the radio-frequency signals received on them similarly amplified, without change of relative phase, and applied to the two pairs of deflecting plates of a cathode-ray oscillograph. In this way the cathode-ray trace gives the relative amplitudes and polarizations of the ground signal and the subsequent echoes in succession. Since the pulses are emitted by the sender at a regular rate (50 per second) it is possible, by means of a suitably synchronized time base, to make the traces corresponding to the ground wave and echoes quasi-stationary on the oscillograph screen so that they may be examined by eye.

---

* This is a curve in which the equivalent path is exhibited as a function of the electric wave frequency.

† The basic idea underlying this method of polarization delineation was independently suggested by Mr R. A. Watson Watt and one of the writers. A very brief account of it has been given in the issue of *The Wireless World*, July 8, 1932, p. 17.

It was found that when the polarimeter was in adjustment the trace corresponding to the ground-wave signal was a straight line, indicating that its magnetic vector was linearly polarized. When downcoming waves from the upper region were also received it was found that in the day-time, when splitting was not in evidence, the echoes were of variable elliptical polarization with a predominantly left-handed rotational sense. When the echo consisted of a normal doublet, it was found that the components were approximately circularly polarized, the component of lesser delay being right-handed and that of greater delay left-handed[*]. (It was possible at times to note this effect up to echo doublets of the fifth order.) These experiments therefore confirmed directly our first interpretation of the nature of split echoes.

§ 3. THEORETICAL EXPLANATION AND DISCUSSION OF RESULTS

(*a*) *The magneto-ionic theory of wireless propagation.* In a discussion on "Atmospheric ionization" before the Society in November 1924[†] it was pointed out by one of the authors that if the conductivity of the upper atmosphere is due to electrons (and not to ions of molecular mass) the propagation of wireless waves in the ionosphere is very considerably influenced by the earth's magnetic field. Gyroscopic terms in the dispersion equations, not considered in the ionic refraction theories of Eccles[‡] and Larmor[§], become of importance, and many of the phenomena familiar in magneto-optics are to be expected. This magneto-ionic theory, as the revised treatment was called, has been developed mathematically, for the general case of propagation at any angle relative to the earth's field, by Appleton[||], Goldstein[¶] and Hartree[**].

On the experimental side Appleton and Ratcliffe[††] have found that downcoming waves 400 metres in length are approximately circularly polarized with a left-handed sense of rotation in England, whereas Green[‡‡] has shown that, under exactly comparable conditions in the southern hemisphere, the downcoming waves are of opposite rotational sense. Such results have been explained as being due to the differential absorption of the two components of opposite rotational sense which travel in an ionized medium under the influence of the earth's magnetic field, the absorption of the right-handed component being much greater than that of the left-handed component for waves of 400 m. travelling in a direction making an acute angle with the imposed field (e.g. for downward propagation in England). But according to the theory already developed, this differential absorption of the magneto-ionic components should be the less marked the shorter the wave-length, so that for short waves we might expect to observe them both with comparable amplitude.

---

[*] The rotational sense was found by advancing or retarding the phase of the signals received on one of the loops (by altering slightly the circuit tuning) and noting the effect on the circular traces on the oscillographic screen.

[†] E. V. Appleton, *Proc. Phys. Soc.* **37**, 22 (1925); see also Nichols and Schelleng, *Bell System Technical Journal*, **4**, 215 (1925).

[‡] *Proc. R. S.* A, **87**, 79 (1912).

[§] *Phil. Mag.* **48**, 1025 (1924).

[||] *Proc. U. R. S. I.* (Washington, 1927).

[¶] *Proc. R. S.* A, **121**, 259 (1928).

[**] *Proc. Camb. Phil. Soc.* **27**, 143 (1931).

[††] *Proc. R. S.* A, **117**, 576 (1928).

[‡‡] *Nature*, **128**, 1037 (1931).

The problem is perhaps best illustrated by taking a practical case of the reflection of, say, 80-metre waves at vertical incidence. We consider the propagation of the waves vertically downwards at an angle of $(\frac{1}{2}\pi - \delta)$ to the magnetic field, δ being the angle of dip. For such a case the relation between the imposed field, δ
its components, and the direction of propagation are as illustrated in figure 4. Here the magnetic field components, transverse and longitudinal to the direction of propagation, are represented by H_T and H_L respectively. H is the total magnetic force.

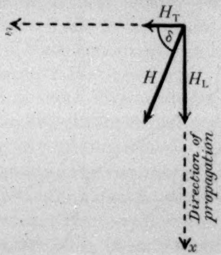


Figure 4. (The y axis is at right angles to the paper.)

For such conditions the dispersion equation relating the refractive index μ to μ
the angular frequency p may be written p

$$\mu^2 = 1 - \frac{2p_0^2}{2(p^2 + \frac{1}{3}p_0^2) - \dfrac{p^2 p_T^2}{p^2 - \frac{2}{3}p_0^2} \mp \sqrt{\left(\dfrac{p^4 p_T^4}{(p^2 - \frac{2}{3}p_0^2)^2} + 4p^2 p_L^2\right)}} \quad \ldots\ldots(1),$$

where $p_0^2 = 4\pi Ne^2/m$; $p_T = H_T e/mc$; $p_L = H_L e/mc$. Here N is the number of N
electrons, of charge e and mass m, per cm³ and c is the velocity of electromagnetic e, m, c
radiation in free space. This equation is valid for negligible or very small friction. The formula with the upper sign refers to the extraordinary ray and that for the lower sign to the ordinary ray. It should be noted that p_0^2 is proportional to the ionization-content N. The corresponding formula for the polarization is

$$\frac{H_y}{H_z} = \frac{ipp_L(1 - \mu^2)}{(1 - \mu^2)(p^2 + \frac{1}{3}p_0^2) - p_0^2} \quad \ldots\ldots(2),$$

where the appropriate value of μ^2 is inserted from (1).

A curve illustrating the relation between μ^2 and N for a case of the propagation of 80-metre waves vertically downward in South-east England has been kindly drawn for us by Miss A. C. Stickland of the Radio Research Station, Slough, and is reproduced in figure 5.

(*b*) *The two types of magnetic splitting and their occurrence.* Now in the pulse measurements in which the doubling of echo signals has been most studied, we are concerned with the separate arrival in time of the two components. Such a group separation of the components can readily be seen to occur in two ways.

We see from the above curve relating μ^2 to N that the refractive index of the extraordinary ray is diminished to zero for a lower value of N than is the case with the ordinary ray*. This means that, for a layer the ionization of which increases with height, the reflection of waves at vertical incidence will take place at a lower level for the extraordinary ray than for the ordinary ray. Because of this we should expect echo pulses associated with the ordinary ray to arrive back at the ground a little behind the other component in time. Such a result is found in the most common type of splitting, and since it arises from the way in which the ionization in the upper atmosphere is stratified we call it "stratification splitting."

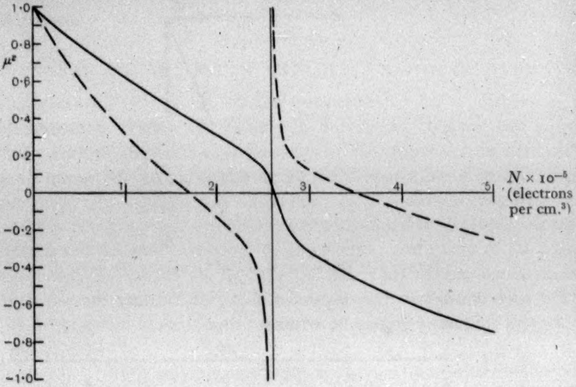


Figure 5.

– – – extraordinary ray (μ_2)
——— ordinary ray (μ_1)

(N, μ^2) curves for $\lambda = 80$ metres. (Infinity of μ_2 at $N = 2{\cdot}58 \times 10^5$. Zero of μ_1 at $N = 2{\cdot}62 \times 10^5$.)

There is, however, another possible way in which the separation of the two components may take place. It is known that there are two ionized regions in the upper atmosphere and that, owing to the fact that the ionization in the upper region may be more intense than that in the lower region, waves which have penetrated the lower region may still be reflected by the upper region. In passing through the lower region, however, any signal pulse is retarded owing to the fact that the group velocity in an ionized medium is less than that in free space. In the case of the two magneto-ionic components, moreover, such group retardation will be differential, and it may be shown from the dispersion formula given above that the group velocity of the extraordinary ray is, for the special conditions in which we are interested, less than that of the ordinary ray. The effect of electron ionization in the Kennelly-Heaviside layer (lower region) is thus to make the extraordinary component lag in time behind the ordinary component. "Group-retardation splitting," as this type of separation may be termed, therefore tends to produce the opposite effect to that produced by "stratification splitting," for stratification splitting retards the ordinary component behind the extraordinary component while group-retardation splitting produces just the reverse effect.

---

* For the extraordinary ray μ^2 first becomes zero when $p_0^2 = \frac{3}{2}(p^2 - pp_H)$, while the same condition is reached for the ordinary ray when $p_0^2 = \frac{3}{2}p^2$.

It has already been noticed that the group-retardation effect due to the ionization in region E suffered by waves which are ultimately reflected by the upper region F is most marked for frequencies just above the critical range of values for which penetration of the lower region begins to take place. We should therefore expect group-retardation splitting to occur most readily for these same experimental conditions. This has actually been found to be the case in experiments carried out with the radio-polarimeter, and these conditions are, as a matter of fact, the only ones under which we have observed splitting of this type. More usually the effect of group-retardation splitting is more than neutralized by that of stratification splitting, so that the first echo-component experienced is right-handed and the second component left-handed in rotational sense.

The dispersion curves illustrating the variation of μ^2 with N immediately show that a greater value of electron-concentration is required for the ordinary ray than for the extraordinary ray to produce the condition $\mu^2 = 0$ which we associate with reflection at vertical incidence. We have, in early morning tests, repeatedly found examples of this. The ionization is at that time increasing owing to the influence of the sun, and we find that, after electron-limitation has been causing the absence of echoes during the night, the shorter delay component is first noted and is then followed a few minutes later by the appearance of the second component. After this had been observed we were able to change to a shorter wave-length and see the process repeated.

In our attempts to determine the frequencies which just penetrate the upper region at different times of the day, we have often had occasion to obtain data from which a curve illustrating the relation between the equivalent path of the atmospheric waves P' and the frequency f could be drawn (see for example figure 1). These f
curves show that for a given value of N the ordinary ray of one frequency, say f_1, f_1
just penetrates the upper region while, at the same time, the extraordinary ray of another frequency f_2 has reached similar critical conditions. f_2
Now while, as has previously been mentioned, it is difficult to say exactly what are the deciding factors which determine reflection, we are fairly clear that the conditions for reflection must approach those indicated by $\mu = 0$. But for frequencies greater than the characteristic gyro-frequency f_H (i.e. $He/2\pi mc$) the condition $\mu = 0$ is reached f_H
for the extraordinary ray of frequency f_1 when

$$N = \frac{3}{2}\frac{\pi m}{e^2}(f_1^2 - f_1 f_H) \qquad \ldots\ldots(3),$$

whereas the same condition is reached for the ordinary ray of frequency f_2 when

$$N = \frac{3}{2}\frac{\pi m}{e^2}(f_2^2) \qquad \ldots\ldots(4).$$

The two frequencies must thus be connected by the relation

$$f_2^2 = f_1^2 - f_1 f_H$$

or

$$(f_1 - f_2) = f_H \left(\frac{f_1}{f_1 + f_2} \right) \qquad \ldots\ldots(5).$$

Since the frequency-difference $(f_1 - f_2)$ is small we see that it is approximately equal to $\frac{1}{2} f_H$ or to about 0·70 Mc./sec. Now it is one of the striking facts of the experimental results that in all the (P', f) curves we have drawn in which the electron-limitation effect for the two components is shown, the frequency-difference corresponding to $(f_1 - f_2)$ is always of this order of magnitude, the mean experimental value for a large number of curves being 0·80 Mc./sec. We believe therefore that this agreement between theory and experiment is additional evidence in favour of the magneto-ionic theory.

The application of the magneto-ionic theory to the explanation of phenomena associated with the reflection of waves from region *E* has not proved so easy of interpretation as in the case of region *F*. It is known that, in general, waves reflected from the lower region are predominantly of left-handed polarization, and this has been attributed to the more marked absorption of the right-handed component during the passage of the waves through the lower and more attenuating part of the ionized region, which is situated below that at which the waves are reflected. The question whether the refractive process causes separation of the ordinary and extraordinary rays by stratification splitting in region *E*, in a manner similar to that found in the case of region *F*, is more difficult to settle. The ionization-gradient in region *E* appears to be greater than that in region *F*, so that simple stratification splitting as indicated by the temporal separation of the two components does not show up so readily. It can, however, be stated that splitting which appears, in the ordinary cathode-ray oscillographic delineation of echoes, to be of exactly the same type as that experienced for region *F* has been noted on many occasions, but we have not yet been able to make definite determinations of the sense of polarization of the two (or more) components separately. Certain phenomena noted under special circumstances, however, assume importance in this connexion. As has been described for reflection from region *F*, the effect of electron-limitation in a case in which the ionization is steadily decreasing is to cause the polarization to change from the predominantly left-handed rotational sense (when the polarization is determined by the greater amplitude of the ordinary ray) to the right-handed sense (when, owing to electron-limitation, the ordinary ray has penetrated the layer and only the extraordinary ray is being reflected). During sunset runs we have also sometimes found this to be the case for region *E*. Using a constant frequency the polarization of waves has at first been left-handed and later, as the ionization has decreased, has become right-handed. As the ionization has further decreased even the extraordinary ray has finally no longer been reflected, and full penetration of the lower region has taken place. Because of these magneto-ionic effects in cases of reflection from the lower region, and of the existence of group-retardation splitting for waves reflected by the upper region, we conclude that the Kennelly-Heaviside layer contains a considerable proportion of free electrons.

(*c*) *The effects of friction.* The expression (1) above for the refractive index of an ionized medium under the influence of an imposed magnetic field was derived for assumed non-dissipative conditions. When account is taken of the collisional friction suffered by the vibrating electrons the value of the refractive index cq, which is now complex, is given* by

cq

$$(cq)^2 = \left(\mu - \frac{i\kappa c}{p}\right)^2$$

$$= 1 - \frac{2p_0^2}{2\left(p^2 + \frac{1}{3}p_0^2 - ip\nu\right) - \dfrac{p^2 p_T^2}{p^2 - \frac{2}{3}p_0^2 - ip\nu} \mp \sqrt{\left(\dfrac{p^4 p_T^4}{(p^2 - \frac{2}{3}p_0^2 - ip\nu)^2} + 4p^2 p_L^2\right)}} \qquad \text{......(6).}$$

where μ is now the real part of the refractive index, κ the absorption coefficient and ν the frequency of the electron collisions with gas molecules. As in (1), the upper sign refers to the extraordinary ray and the lower sign to the ordinary ray.

μ, κ

ν

The corresponding formula for the polarization is

$$\frac{H_y}{H_z} = i\left\{\frac{2p_L\left(p^2 - \frac{2}{3}p_0^2 - ip\nu\right)}{pp_T^2 \pm \sqrt{\{p^2 p_T^4 + 4p_L^2\left(p^2 - \frac{2}{3}p_0^2 - ip\nu\right)^2\}}}\right\} \qquad \text{......(7).}$$

The two formulae (6) and (7) are therefore the most general representative equations of the magneto-ionic theory in terms of a ray treatment, and their elucidation and application constitute one of the chief problems of present-day wireless propagation theory. We can here only mention a few of the more salient deductions which can be made from them.

In the first place (6) and (7) yield, as they should, formulae identical with those given by Lorentz for the special cases of transmission longitudinal and transverse to the imposed magnetic field. They also show that, for vertically downward propagation in South-east England at an acute angle with the earth's magnetic field, as in our present problem, the left-handed component is less absorbed than the right-handed component.

When friction is taken into account it is also possible to explain a difficulty which arises in the elucidation of the formulae obtained when friction is neglected. For the purely longitudinal type of propagation it is found from (1) that the refraction index of the extraordinary ray becomes zero when $p_0^2 = \frac{3}{2}(p^2 - pp_H)$, while the same condition is reached for the ordinary ray when $p_0^2 = \frac{3}{2}(p^2 + pp_H)$. Both ordinary and extraordinary rays are, moreover, in this case circularly polarized for all values of p_0^2. For all other directions of propagation, however, as has been mentioned above, the refractive index of the medium becomes zero for the extraordinary ray when $p_0^2 = \frac{3}{2}(p^2 - pp_H)$ and when $p_0^2 = \frac{3}{2}(p^2 + pp_H)$, while the same condition is reached for the ordinary ray when $p_0^2 = \frac{3}{2}p^2$. In the propagation transverse to the magnetic field the linear polarizations are maintained for all values of p_0^2, but for intermediate directions the polarizations change as the waves travel into regions of different p_0^2. For very small and very large ionizations (that is for small and large values of p_0^2) the polarizations of both components are circular, but in the region from $p_0^2 = \frac{3}{2}(p^2 - pp_H)$ to $p_0^2 = \frac{3}{2}(p^2 + pp_H)$ rapid variations take place, the polarizations of both ordinary and extraordinary rays being linear when $p_0^2 = \frac{3}{2}p^2$. We therefore see that, when friction is neglected, longitudinal propagation stands out as a special case, in that there are only two values of p_0^2 for which the refractive index becomes zero whereas for all other directions there are three.

---

* Appleton, *J. Inst. E. E.* 71, 642 (1932).

A more detailed examination of the general formulae (6) and (7), in which friction is taken into account, shows that there is no real discontinuity between the longitudinal and the other cases. It is found that the nature of the type of friction is determined by the value of $2p_L \nu/p_T^2$, a quantity which depends on the direction of propagation, the collisional friction and the earth's magnetic intensity. When the value of this quantity is small compared with unity, the propagation resembles more closely the transverse type. The polarizations then become plane for the conditions $p^2 = \frac{2}{3}p_0^2$, while the refractive index for the ordinary ray approaches zero at the same point. On the other hand, when $2p_L \nu/p_T^2$ is large compared with unity the propagation resembles more nearly the purely longitudinal type. The polarization does not then become plane for the conditions $p^2 = \frac{2}{3}p_0^2$, nor does the refractive index of the ordinary ray approach zero for the same conditions.

These considerations have a bearing on a question which has been discussed above. If the propagation, for conditions under which reflection takes place, resembles the transverse type, we have seen in equation (5) that the frequency difference $(f_1 - f_2)$ between the two frequencies which penetrate the region as extraordinary and as ordinary waves is equal to $f_H f_1/(f_1 + f_2)$. If, however, the critical ratio $2p_L \nu/p_T^2$ is much greater than unity, it is easy to show that under these conditions, which approximate to longitudinal propagation, the frequency difference $(f_1 - f_2)$ now becomes equal to f_H or to 1·32 Mc./sec. The corresponding theoretical value for propagation resembling the transverse type, as has been shown, is about 0·70 Mc./sec., while the value obtained experimentally for the upper region is 0·80 Mc./sec. Our knowledge of the values of ν at various heights is somewhat uncertain, but there is little doubt that for the upper region, where ν must be numerically 10^3 or less, we are dealing with a case approximating to the transverse type. The experiments support this, since the experimental value of $(f_1 - f_2)$ is much closer to the transverse value of 0·70 Mc./sec. than to the longitudinal value of 1·32 Mc./sec. For the lower ionized region, where ν may be considerably higher, it does not appear possible yet to make any such corresponding decision with great certainty.

(*d*) *The limiting polarization of wireless waves as observed at the ground.* It seems reasonable to assume that the polarization of waves received at the ground is the same as that which they possess when travelling through the lowest part of the ionized region from which they have emerged. For comparison with our experimental results, therefore, we require to find the polarization for small ionization. Putting p_0^2 equal to zero in (7) we find

$$\frac{H_y}{H_z} = i\left\{\frac{2p_L(p - i\nu)}{p_T^2 \pm \sqrt{\{p_T^4 + 4p_L^2(p - i\nu)^2\}}}\right\} \qquad \ldots\ldots(8).$$

Further simplification of this formula depends on whether we have $p \gg \nu$ or $p \ll \nu$ for the region in which ionization falls to a low value. In the former case we have

$$\frac{H_y}{H_z} = i\left\{\frac{2pp_L}{p_T^2 \pm \sqrt{(p_T^4 + 4p^2p_L^2)}}\right\} \qquad \ldots\ldots(9),$$

while in the latter case

$$\frac{H_y}{H_z} = \left\{\frac{2p_L\nu}{p_T^2 \pm \sqrt{(p_T^4 - 4p_L^2\nu^2)}}\right\} \qquad \ldots\ldots(10).$$

For our present case of the propagation of 80-metre waves vertically downwards in South-east England we have either in case (9) or in case (10) polarizations which are very nearly circular. It is not until propagation is nearly at right angles to the earth's magnetic field that we find the limiting polarizations tending to change over to the linear state. We thus find that the experimentally observed circular polarizations are such as are to be expected from the theory.

If we compare the limiting polarizations with the characteristic polarizations which obtain at the regions of higher ionization where the waves are reflected, we are able to explain how it is that the extraordinary ray component F_1' is usually less distorted than is the ordinary ray component F_1''. For all values of the quantity $2p_L\nu/p_T^2$, such as we have to deal with in vertical propagation in South-east England, the polarization of the extraordinary ray alters but little in its passage into and out of the ionized region. On entry it is circularly polarized, while, for the condition $p_0^2 = \frac{3}{2}(p^2 - pp_H)$ when it is reflected, we have $H_y/H_z = ip_L/p_H$, which means that the polarization is still not very far from circular. The extraordinary ray travels therefore almost unaltered in polarization, as in the purely longitudinal type of propagation. On the other hand, matters are quite different for the ordinary ray. When this ray enters the ionized region it is circularly polarized and, unless $2p_L\nu/p_T^2$ is large, its polarization alters rapidly with increasing ionization*. Such alteration can only take place as a process of re-splitting. Under conditions of low ionization-gradient such re-splitting will be attended with an increase in the temporal duration of the signal pulse. This result will also be emphasized by a process of partial internal reflection, which is easily seen to be possible between the regions at which the refractive index becomes zero. An additional, though perhaps not predominant, effect may be due to the fact that, when dP'/df is large, the component frequencies of the pulse itself are very much separated, with consequent distortion. When both components are present this effect will, in general, be greater for the ordinary than for the extraordinary ray. Departures from a smooth ionization-gradient doubtless add to the complexities of the pulses, while temporal changes in N and H cause the rapid intensity-variations of the distorted pulses which are experienced at almost all hours of the night.

F_1'
F_1''

---

* If $2p_L\nu/p_T^2 < 1$ the polarization changes from circular to linear.

§4. ACKNOWLEDGMENTS

The work described in this paper was done as part of the programme of the Radio Research Board of the Department of Scientific and Industrial Research. The experiments were carried out partly at King's College, London, and partly at the Radio Research Station, Slough, and we wish to express our indebtedness to Mr R. A. Watson Watt, the Superintendent of that station, for his kind collaboration in part of the experiments and also for his helpful advice and discussion at all stages of the work. We also wish to thank Mr J. F. Herd, Mr L. H. Bainbridge-Bell and Mr R. Naismith, of the Radio Research Station, for their assistance in the course of the experiments.

While the work has been in progress we have enjoyed the great advantage of being able to compare our results with those obtained by Messrs J. A. Ratcliffe and E. L. C. White of the Cavendish Laboratory, who were at the same time investigating similar problems by a different method which they had independently devised.

DISCUSSION

Mr R. A. Watson Watt. The authors have carried one important stage further the description and explanation of the increasingly complex phenomena of ionospheric reflection which are revealed by increasingly powerful observational methods applied over extending ranges of time-of-day and season. The clarification of the conditions for "stratification splitting" and for "group-retardation splitting" and the discussion of the relative complexity of the echo pattern for the ordinary ray-component F_1'' are specially valuable features of the present communication.

Mr R. H. Barfield. I think it would be of great interest to have some statement of the relative frequency of occurrence of the two types of echo pattern illustrated in figures 2 and 3 respectively. Is the possibility that scattering, as opposed to magneto-ionic splitting, might be an important cause of the phenomena of figure 3 completely excluded?

Authors' reply. In reply to Mr Barfield's first question we can only say that distorted echoes are almost always found under conditions where electron-limitation of amplitude is operative. This applies to both ordinary and extraordinary rays. As we have mentioned in the text, a low ionization-gradient favours the formation of complex multiplets.

The fact that all parts of a distorted echo show definite circular polarizations, of one sign or the other, appears to rule out any explanation in terms of scattering alone, the magnetic field of the earth being neglected. The complex echoes with their ceaseless amplitude-changes may be taken as expressing the disorderliness of the electron distribution. We do, however, believe that each part of a complex echo represents partial reflection from a part of the medium which is large compared with a vacuum wave-length, so that, to that extent, we rule out scattering as usually understood in optics.

621.396.2.029.1:551.594.11

THE GENERATION AND RECEPTION OF WIRELESS SIGNALS OF SHORT DURATION

By J. F. HERD, A.M.I.E.E., Radio Research Station, Slough

Communicated by R. A. Watson Watt, September 15, 1932. *Read December* 2, 1932.

ABSTRACT. In the use of short-duration signals for investigation of the ionosphere, it is convenient to emit the signal pulses at a controlled rate and to receive them on an oscillograph giving temporal discrimination between the arrival of the ground ray and that of subsequent echoes. Simplification of recording technique can be obtained if, at the receiver, an oscillograph of the cathode-ray type is used in conjunction with a time-scale voltage whose rate of recurrence is exactly the same as that of the emitted impulses. The paper describes methods of utilizing the common frequency of an a.c. supply network to secure such synchronization.

The arrangement is first described in connection with ticking-grid circuits at the emitter and as a linear time-base device at the receiver. Alternative linear time bases using mercury-vapour triodes (thyratrons) are then discussed, and these circuits are combined with known means of obtaining a circular time scale to produce a spiral time scale affording wide temporal separation of observed phenomena and more fully utilizing the whole oscillograph screen. Lastly an improved method of impulsing the transmitter is described, involving the use of a thyratron as an abrupt switching device.

§ 1. INTRODUCTION

The use of wireless signals of short duration is already well known as a means of investigating the conditions of the ionosphere.

In a recent communication Prof. E. V. Appleton and Mr G. Builder* have described a simple method of generating radio-frequency impulses of short duration. The method utilizes the fact that in an oscillating triode generator, if a suitable condenser-resistance combination be inserted in the grid circuit as shown at *CR* in figure 1, the triode generates oscillations in the form of brief impulses alternating with periods of quiescence whose duration is of the order of 25 or more times that of the duration of the oscillatory train. The same circuit has also been used for the production of a time base for use with a cathode-ray oscillograph†. During the period of oscillation a voltage is built up across the condenser *C* abruptly driving the fluorescent spot to the left of the screen, when the spot proceeds to return from left to right in a slower leakage-time of the relative order stated. With a condenser-resistance combination the left-to-right travel occurs exponentially, but can be made linear by the use of a saturated diode in place of the ohmic resistance.

The reception of such short-duration impulses provides a method for determination of the time between the arrival of a ground-ray signal and that of one or more signals returning from the ionized layer. In this application, it is convenient, as is stated in the paper by Appleton and Builder, to make visual observations on a cathode-ray oscillograph, with photographic recording with an oscillograph either of this type or of the electro-mechanical or Duddell type. For visual observation with the cathode-ray oscillograph it is desirable to hold the time base so that its recurrence-frequency agrees exactly with the pulse-frequency of the radiated oscillation. In this case the ground-ray signal always falls on the same place in the left-to-right travel of the fluorescent spot, with the indirect-ray signals following after it in each sweep according to their continuously varying conditions which are the subject of investigation. For photographic recording a convenient and economical method is to use the same general arrangement and take snap exposures at suitable intervals of the varying conditions of the indirect-ray signals.

---

* *Proc. Phys. Soc.* **44**, 76 (1932).

† *Proc. R. S.* A, **111**, 672 (1926).

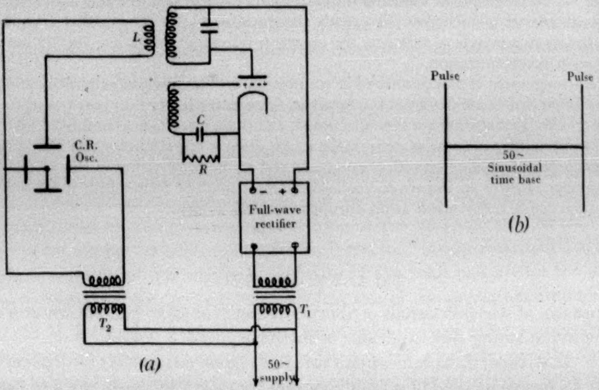


Figure 1. *a.* Method of locking transmitter to half-waves of voltage supply. *b.* Typical screen image when pulse-recurrence is locked to rectified half-waves of supply voltage.

With a suitable fluorescent material (e.g. calcium tungstate) on the oscillograph screen and by means of a camera of simple type, it is possible to obtain snap photographs with exposures of the order of from 0·2 to 0·1 sec., which give a record whose depth and quality are adequate for analysis. Moreover the use of the cathode-ray oscillograph for this purpose has the advantage that the same device serves both for monitoring and for photography. In addition, the monitoring indication remains visible during the recording process, while the photographic recording can be brought into instant operation either at regular intervals or at any special moment justified by the conditions.

For satisfactory photography, it is necessary that the image on the fluorescent screen should remain absolutely stationary. It is therefore essential that the recurrence-frequency of the time-base stroke should agree most accurately with the pulse-frequency of the transmitter. While it is possible to achieve a fair approach to a stable pattern by manual control, e.g. at the receiver, some form of locking or master-control appears to be desirable. The use of frequency-controlled 50 ~ supply mains at both transmitter and receiver suggested itself as a means of impressing a stable frequency on the recurrence at both ends, and this paper describes simple methods which appear satisfactory for the purpose and have several points of novelty at both transmitter and receiver.

§2. CONTROL OF PULSE-GENERATION

The method consists essentially in using an unsmoothed supply, either from unrectified alternating current or from the unsmoothed output of a full-wave rectifier fed from the a.c. supply mains to energize the anode circuit of the valve and cause the signal pulse to recur at the same point in successive cycles of the supply voltage. The arrangement was first tried on a laboratory scale, in the conditions described below, and proved completely satisfactory in giving the desired locking state. Modifications for operating at higher power-levels are discussed later in the paper.

In order to utilize the higher frequency, namely 100 ~, both of signal pulses and of time-base recurrence, the second-mentioned arrangement (using unsmoothed rectified half-waves) was first tried. The local transmitter consisted of a simple coupled-circuit oscillator with grid condenser C and resistance R for control of the pulse-frequency. The usual smooth d.c. supply to the anode circuit was replaced by the unsmoothed supply from a full-wave rectifier, as shown in figure 1 *a*.

A convenient method of adjusting the transmitter is also shown in figure 1. Values of C and R were first set so as to give approximately the desired frequency-recurrence of 100 per second. A coil L loosely coupled to the oscillating circuit impressed the transient trains of oscillations on one pair of plates of a cathode-ray oscillograph. The other pair of plates was supplied with a timing voltage of 50 ~ by a small transformer T_2. It was then found quite easy to adjust the CR value (the variable element was actually the condenser C) until a perfectly steady picture of the type shown in figure 1 *b* was obtained. As synchronization was approached the picture fell into a pattern in which the impulses moved jerkily towards the outer ends of the time-base line showing increasing amplitude as the impulses approached the ends. On final adjustment the impulses fell exactly at the ends of the base-line, as shown in figure 1 *b* and were then of the maximum amplitude observed, showing, presumably, that the incidence of the oscillation-train agreed exactly with the peak of the supply voltage from the full-wave rectifier. With this adjustment, the picture remained locked for very long periods and there appeared to be no difficulty either in keeping it perfectly stationary or in reproducing the conditions from day to day.

§3. LOCKING THE RECEIVER TIME BASE

In the case of the time base at the receiver, the same general method was employed with complete success, viz. to feed the anode of the oscillating circuit by means of the unsmoothed output of a full-wave rectifier. The modifications made in the time-base circuits were very minor and consisted merely in substituting this unsmoothed supply for the normal battery supply of the oscillator (after removal of a by-pass condenser that was actually installed), while still leaving the battery connected to the diode for the purpose of maintaining the improved linearity which this confers.

The behaviour of the time base was then somewhat peculiar, and a little explanation of the phenomena observed is called for. The condenser was set to a value which was known to give, in conjunction with a suitable diode brightness, a good measure of linearity in the main stroke. As a timing reference, the 50 ~ supply was fed to the vertical plates via a small transformer in order to study the behaviour of the horizontal time-base stroke. The diode was then started at a dull glow and gradually brightened. It was very noticeable that the pattern showed a marked tendency to lock on the sub-multiples of 50 ~ through which the time base then passed in the course of this adjustment. Thus it was very easy to obtain a stationary picture of 2 : 1, 3 : 2 and finally 1 : 1 when the time base was exactly of the duration $\frac{1}{50}$ sec. As the diode was continuously brightened, the picture tended finally to fall rather sharply into the pattern of 1 : 2 as shown in figure 2 *b*, which shows the time base of $\frac{1}{100}$ sec., breaking the 50 ~ voltage into its two half-cycles.

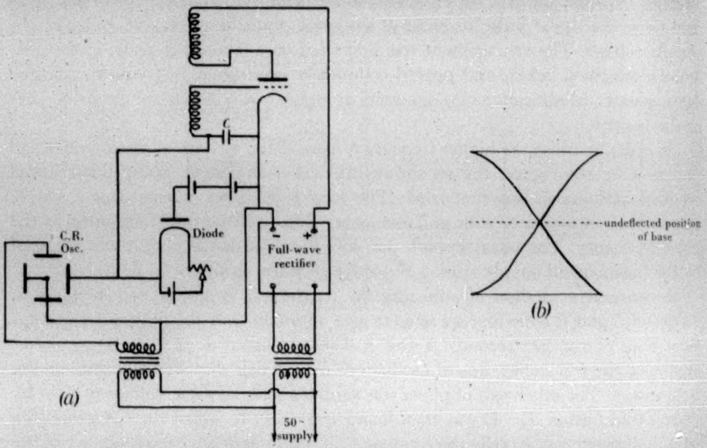


Figure 2. *a*. Method of locking receiver time base to half-waves of voltage supply. *b*. Typical screen image when time base is locked to rectified half-waves of supply voltage.

The setting which gave this stationary image of half-cycles was found to be the optimum for operation. Further brightening of the diode beyond this point introduced complicated effects and patterns which were extremely difficult to interpret and might be misleading. Fortunately there was no need ever to use these, since the arrival at the condition indicated was very definite and unmistakable, and represented the condition desired for the stationary pattern of the received pulses.

With the time base adjusted in this manner, the circuit of figure 3 *a* was then used, and it was found that a perfectly stationary picture of the pulses was immediately obtained.

As a matter of interest the effect was then examined of connecting the time base to the successive phases of a 3-phase supply, leaving that of the transmitter fixed so as to simulate the conditions that might be met with in practice. The results were as shown in figure 3 *b*, the pulse picture moving along the base with each phase. Actually when the transmitter and time base were fed from what was known to be the same phase, the resultant picture was the last of those shown. If, therefore, in a practical system utilizing this scheme this particular picture should result, it would be easy at the receiving end to change the phase of the supply serving the time base so as to place the picture at a more suitable position, e.g. that occupied by the first picture in figure 3 *b*, in order to get the optimum conditions for observation of echoes following the reception of the ground-ray signal. In these experiments the pulses applied to the oscillograph were the radio-frequency trains derived from the coil L coupled to the oscillator as in figure 1 *a*. The pulses thus appear on both sides of the time base as shown in figure 3 *b*.

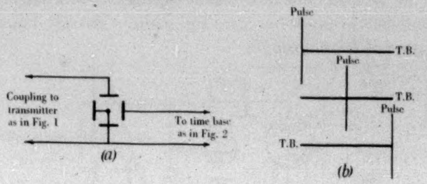

Coupling to transmitter as in Fig. 1
To time base as in Fig. 2
(a)
Pulse
T.B.
Pulse
T.B.
Pulse
T.B.
(b)

Figure 3. *a*. Circuits for checking locking of transmitter against similarly locked time base. *b*. Location of pulse as different phases of 3-phase 50 ~ supply are used for time base.

With the optimum adjustment of the time base, as in figure 2, there may be a slight tendency for successive strokes of the time base to be slightly unequal owing to inequalities of successive half-waves of the supply. This condition is very evident by visual inspection, the lowered luminosity of the excess length of one stroke being obvious. If this is observed it can be remedied by the insertion of resistance in one limb until the time base is clearly of equal luminosity over its length.

§4. USE OF UNRECTIFIED A.C.

Later exactly similar arrangements were applied in the case where both local-transmitter and receiver time-base circuits were fed with unrectified alternating current. The half-wave rectifier was omitted in each case, and the transformer was applied directly to the anode circuit of the oscillating triode, so that the valve was energized only during those half-cycles which rendered the anode positive. It was then, of course, necessary to adjust the CR circuit at the transmitter and the corresponding condenser-diode circuit in the receiver time base to the duration of $\frac{1}{50}$ sec., when it was possible to obtain exactly the same locking phenomena as are described above for the case of supply by rectified half-waves.

The experiments described above were all conducted on a laboratory-test scale, and appeared perfectly satisfactory. When an attempt was made subsequently to apply similar methods to transmitters of higher power, difficulties were encountered which led to modifications described later in this paper.

§5. LOCKED TIME-BASE CIRCUITS USING A MERCURY-VAPOUR TRIODE

A disadvantage of the "ticking-grid" time-base circuit described above is that, in its operation, a fairly high radio frequency is impulsively generated and, even with reasonable precautions, there is a considerable tendency for it or its harmonics to be picked up by the main radio receiver with which the circuit is, in practice, associated. Other methods of locking the oscillograph time stroke on the mains frequency are therefore desirable, and several arrangements have been tried.

A method which has proved very convenient is one using a mercury-vapour triode of the type generically known as the "thyratron." The use of a triode of this type in a self-flashing system has already been described by W. B. Nottingham* and A. L. Samuel†; the arrangement takes advantage of the difference between striking and extinction potentials, somewhat after the manner already known in connexion with self-flashing neon-lamp circuits.

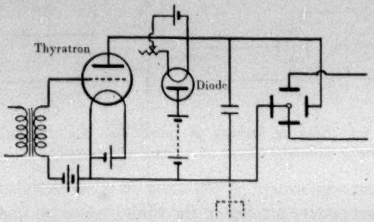


Figure 4. Use of mercury-vapour triode (thyratron) for linear time base.

A convenient modification for use as a general time base of variable frequency consists in the employment of a condenser-diode circuit as shown in figure 4. For observation of a sustained phenomenon, e.g. a steady alternating voltage, locking can be obtained by a light coupling between the grid of the thyratron and the output of the source, as indicated in figure 4. Locking in this manner has been found to give an exceedingly stable pattern, even when the frequency of the vertical phenomenon is many times—e.g. 10 or more times—that of time-base recurrence. Incidentally, it may be mentioned that the coupling necessary to give this locking effect is extremely small. For example, with a transformer of intervalve type in the grid circuit, it has been found sufficient to join only one terminal of the primary to the high-potential terminal of the source under examination. The load imposed on the source can thus be made negligibly small.

---

* *Journal Franklin Institute*, **211**, 751 (1931).

† *Rev. Sci. Inst.* **2**, 532 (New York, 1931).

This arrangement also permits the locking of the time stroke to the recurrence-frequency of $\frac{1}{50}$ sec., as set by 50 ~ mains. This is done by first adjusting the condenser-diode circuit to this period and then feeding into the grid coupling a small component of the 50 ~ mains voltage. The arrangement gives very satisfactory locking which, further, remains adequately locked to this recurrence rate when transients, such as the short-duration radio signals described earlier, are applied to the other dimension of deflection. A notable feature of the arrangement, true at least of the particular mercury-vapour triodes used in these experiments at low frequencies, such as those of the 50 ~ supply mains, is that the ratio of forward to back stroke can be made very short indeed, ratios well over 1000 : 1 having been found possible*.

If, however, the main purpose is to lock the receiver time base at a recurrence-rate governed entirely by the frequency of the a.c. supply, a very convenient arrangement can be obtained by feeding the anode circuit of the thyratron from the a.c. mains. A typical characteristic property of the mercury-vapour triode is that, with a suitable value of negative voltage applied to its grid, relations between anode voltage and anode current can be made to follow a law such as those shown respectively by the dotted lines and heavy lines of figure 5. Expressed generally, according to the grid voltage actually used, it can be arranged that no anode current passes until a certain anode voltage is reached in the positive half of the applied a.c. cycle. Once anode current has thus been started, the applied anode voltage takes charge and the anode current follows the anode voltage until the latter falls to zero, when the grid voltage again takes charge.

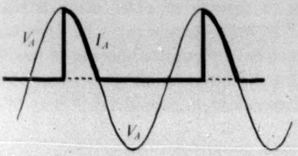


Figure 5. Abrupt rise of anode current in thyratron with suitable grid voltage.

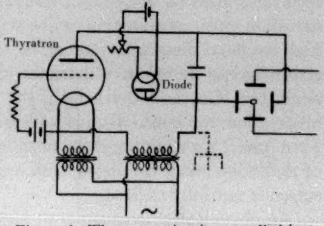


Figure 6. Thyratron circuit controlled by 50 ~ supply mains.

A time-base circuit taking advantage of this principle is shown in figure 6. The negative grid voltage is set to a value such as to give conditions approximating to those of figure 5. The abrupt rise of anode current charges the condenser, which then proceeds to discharge through the diode, giving a typical time-sweep very closely approaching linearity. The condenser-diode circuit is, of course, normally adjusted to $\frac{1}{50}$ second, but the arrangement locks equally well on submultiples of the 50 ~

---

* Certain peculiarities of the thyratron circuit arise when the time base is caused to sweep at higher recurrence-frequencies, e.g. 1000 per second or more. These are due to the definite time taken to de-ionize and are discussed in the paper by W. B. Nottingham already cited (first reference on p. 226).

frequency. Another very valuable feature is that by shortening the discharge-period of the condenser-diode circuit—e.g. by brightening the diode filament—the time stroke can be made to remain recurrent at the rate of 50 per second, but the actual travel across the oscillograph screen can be made in a few milliseconds, with a standstill at the end of the traverse pending the incidence of the next charging impulse. Thus it can be arranged that the timing stroke shall occur in 2 or 3 milliseconds with a standstill for the remaining 18 or 17 msec., the total period being 20 msec. (i.e. 50 ~) recurrence.

This is, of course, of great advantage in giving wide opening of short-duration phenomena, provided that these can be caused to occur in the appropriate first few milliseconds of the time-sweep. To ensure this, some form of phase-control may be necessary, this being most conveniently applied to the anode-circuit voltage supply.

§6. A SPIRAL TIME BASE CONTROLLED AT SUPPLY FREQUENCY

While the above base may be used in the manner described to give a very rapid stroke of controlled recurrence, it has the disadvantage that the remainder of the recurrence interval is lost for observation or recording. If the whole of the phenomenon under examination can be suitably located within the brief moving sweep, high temporal discrimination can be obtained. For example, with an oscillograph screen having an effective diameter of 8 cm., a spacing of 4 cm./msec. is readily attainable. On the other hand if the whole 20 milliseconds must be kept under observation, the same effective screen-diameter only permits a spacing of less than $\frac{1}{2}$ cm./msec. In addition, if the phenomenon under observation gives an amplitude of deflection small compared with screen-dimensions, a considerable part of the screen is not fully utilized.

An obvious improvement is to turn the time scale into a circle using the same effective screen diameter; this confers immediately an improvement of π in temporal discrimination. A circuit providing such a circular time scale has been developed at the Radio Research Station and has recently been described*. The principles of the arrangement are, however, briefly recapitulated here. The circuit is as shown in figure 7. A sinusoidal voltage of frequency n is divided into quadrature components, which are applied to a push-pull modulator of the type first described by Heising. The output from the anode circuits of the valves causes the fluorescent spot to rotate in a circle whose circumference is executed in $1/n$ sec. The phenomenon under observation is introduced as shown at V in figure 7 and serves effectively to modulate the amplitude of the output, thus producing radial departures from the circular trace.

A modification giving still higher temporal discrimination, while preserving the whole of the recurrence-period under observation, consists in converting the circle into a spiral, each of whose turns is $1/n$ sec. in duration while the whole spiral base is N/n sec. in duration, where N is the number of turns in the spiral. In the case where the control is locked to the a.c. mains it is desirable to preserve the whole period N/n at 20 msec., corresponding to a 50-per-second recurrence. n thus becomes most conveniently a double or quadruple multiple of 50, secured by doubling or quadrupling the mains frequency, and a spiral of total length 20 msec., divided into 2 or 4 turns of 10 and 5 msec. respectively, is obtained.

---

* *J. Inst. E. E.* **71**, 82 (1932).

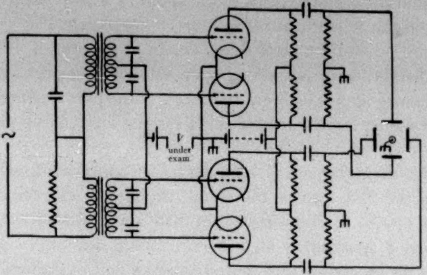


Figure 7. Circuits for circular time base with radial excursion of phenomenon under observation.

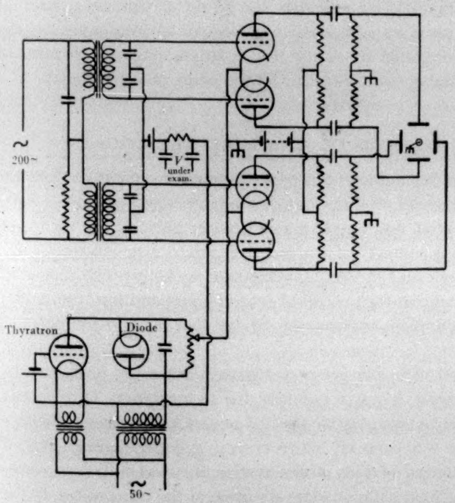


Figure 8.

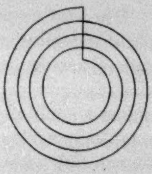


Figure 9.

Figure 8. Modification of figure 7 to give spiral time-scale.
Figure 9. Typical appearance of four-turn spiral controlled by 50 ~ mains.

The modifications necessary are shown in figure 8. Two successive stages of frequency-doubling are used to provide the input frequency to the circular-time-base system, causing the spot to rotate at the frequency of 200 ~. A saw-tooth voltage of 50 ~ is then introduced into the modulating position so that the amplitude of the circular travel is steadily diminished during four revolutions, returning abruptly to its outer position after the manner shown in figure 9. The 50 ~ saw-tooth impulses can conveniently be obtained from a thyratron circuit controlled by the a.c. mains, as described in connection with figure 6. In order to obtain relatively uniform separation between the turns of the spiral, it is convenient to make the saw tooth linear, for instance by the use of a diode. Potentiometric division gives control of the actual amplitude of the inward movement of the spiral. If a relatively low-impedance (i.e. bright) diode is used, a high parallel resistance, used in this manner, still permits adequate approximation to linearity. The phenomenon under observation is introduced at an extra pair of terminals in the modulating position, as shown in figure 8.

It will thus be seen that a very high degree of temporal discrimination can be obtained during the first turn of the spiral, permitting close examination of the incidents of this epoch. By limiting the inward movement of the spiral, approximately as in figure 8, moderately high discrimination can still be preserved during the remainder of the incursion, thus permitting adequate examination of subsequent phenomena.

For many purposes—including, for example, the study of wireless echoes of short delay—a two-turn spiral gives sufficient improvement of time-scale length. This is, of course, readily obtained by using only a single stage of frequency-doubling, the inward travel being still controlled by the main 50 ~ frequency.

§7. AN IMPROVED METHOD OF TRANSMITTER-LOCKING

The work described at the beginning of this paper in connection with the locking of the transmitter to the mains was, as there stated, conducted only on a laboratory scale. Thus the local transmitter was simply a small power valve of the receiving class, energized by anode peak voltages of the order of 200 to 250. In these conditions no difficulty was experienced in obtaining adequate locking which remained completely stable without attention for periods of several hours and was, moreover, reproducible without further adjustment from day to day over three or four days of test observation.

In applying the same method to a larger-power transmitter using peaks of 2 or 3 kV., difficulty was experienced; it was apparently due to insulation, for example in the grid circuit. Thus, while it was possible to obtain exact locking as on the low-power scale, the adjustment was certainly more critical and the maintenance of locking less stable. For prolonged periods of observation this was sufficiently pronounced to be detrimental, at least without some attention at the transmitter, to the main advantage of the system, i.e. to the production of a perfectly stable pattern on the oscillograph screen. The ticking-grid oscillator is naturally a somewhat unstable device, and it is a common experience that, in the absence of an imposed lock, it is liable to variations of recurrence-frequency; and these variations, although possibly very small, may be sufficient to give a drifting pattern on the oscillograph. In photographic recording of the type envisaged, no drift is permissible. The imposition of a lock by the method already described effected a considerable improvement, but minor variations of insulation still permitted the tuned circuit to be triggered into oscillation at slightly differing points about the relatively flat top of the a.c. positive peak-voltage.

In order to improve the conditions, it was thought jointly by Mr G. Builder and the author that advantage might be taken of the property of the thyratron already illustrated in figure 5 and described in connection with the locked time base. In particular, it appeared probable that the abrupt rise of anode current in the thyratron circuit could be made to act as an additional switch or master control, triggering the circuit into oscillation very abruptly at a definite point of the anode-voltage cycle. A thyratron was therefore inserted in series with the anode circuit of the valve, as shown in figure 10. Uncertainty existed as to the exact values of the voltage-drop applied at any instant across the thyratron and valve respectively, especially during their inactive periods, and this rendered it difficult to make any pre-calculation of the voltage necessary to give the appropriate negative grid bias to the thyratron. When a local oscillograph, however, was used as a monitor in the manner already described, no practical difficulty was experienced in obtaining a value of bias which materially improved the locking state, and yielded also another desirable improvement, viz. a shortening of the signal pulse. The value of the bias was not found to be highly critical in adjustment, while the addition of the thyratron was found to confer much greater latitude in the other adjustments, notably those of the condenser-diode combination which was used in the grid circuit as a convenient means of control.

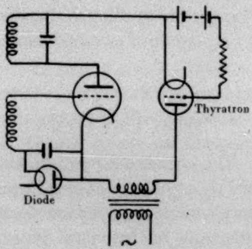


Figure 10. Control of pulse-generation by thyratron as abrupt switching-device.

§8. CONCLUSION

The locking of the transmitter and the oscillograph image represent a matter of considerable importance in any prolonged series of observations using this type of signal for measurements of the ionosphere. While the arrangements discussed by no means exhaust the possibilities of the use of common-frequency supply mains at both stations, they represent methods which are economical in execution and satisfactory in operation. Although they have been described in what is no doubt a particular and perhaps a somewhat limited application, the methods may possibly have other applications in the examination of various types of phenomena, and particularly of transients, where the recurrence of the time base and of the phenomenon under observation can be controlled from a common-frequency source.

§9. ACKNOWLEDGMENTS

The work described in this paper was carried out as part of the programme of the Radio Research Board and is published by permission of the Department of Scientific and Industrial Research. Thanks are due to Mr R. A. Watson Watt, Superintendent, Radio Research Station, Slough, for the initial suggestions in connection with this work and for continued advice during its progress.

DISCUSSION

Prof. E. V. Appleton. The author's contribution to our technique for ionospheric investigations constitutes an important step forward. By putting the burden of synchronization on the employment of a common electric mains supply at sending and receiving station we not only render visual observations of echo portrayals easier but also bring about the possibility of continuous photographic recording. Apparatus designed on the lines described by Mr Herd and built at the Radio Research Station, Slough, was taken out last July to Tromsø in Norway in connexion with the work to be carried out during the International Polar Year, 1932–3. Owing to the fact that the same alternating-current supply was available at Simavik (on the island of Ringvadsø) and Tromsø, which places are 19 km. apart, it was possible to use the author's method of synchronization. The fact that the expedition was able to build its sending and receiving stations on the two islands in question and begin recording within a week of landing at Tromsø is a tribute to the simplicity and reliability of the system.

Mr R. A. Watson Watt. I think the papers by Messrs Herd and Naismith might appropriately be described as "Workshop Notes." They represent two aspects of the forging and testing of appropriate tools for the investigation of the ionosphere. This general investigation is not a "wireless" one in the sense that it is of interest only to the communications engineer. Ionospheric research is an important branch of the general physics of the earth, of that wider "geophysics" whose title is tending to be, somewhat unfortunately, usurped by the applications of a small branch of the subject.

Technical tricks, such as those described by the author, are of extreme importance where it is necessary to amass large quantities of observational material; the reduction of the material is so much more laborious than is the mere recording that every effort must be made to carry out recording in the form which makes reduction easy and expeditious. The methods here described are being applied very successfully to this end in the special Polar Year work which the Department of Scientific and Industrial Research, with the co-operation of the National Committee for the Polar Year and of King's College, London, is carrying out within the Arctic Circle and in this country. But I have no doubt that the very neat and effective devices described by the author will find applications in other fields, and not only in those where "wireless" problems are in question.

The author has perhaps erred on the side of modesty in failing to indicate that he was very directly concerned in the second reference which he gives at the foot of p. 221.

Mr P. W. WILLANS. I was interested in a remark made by the author on the inequality of the time-base strokes in one of his synchronizing arrangements. He attributes this inequality to the fact that his full-wave rectifying device was not operating with strict symmetry. My experience has been that a similar effect may be produced as a result of the nature of the impedance in the anode circuit of the "ticking oscillator" valve. In the course of some attempts to make a ticking oscillator produce pulse wave-forms of various shapes in its anode circuit I more or less accidentally inserted a tuned circuit of high efficiency in this circuit, the resonant frequency being some six or seven times the low-frequency characteristic of the ticking oscillator. A somewhat astonishing result was obtained, in that two alternating trains of dissimilar damped waves were set up in the tuned circuit, the effect being readily observable on a cathode-ray oscillograph. One train started from a larger amplitude than the other and the impulse at the end of the first train gave rise to a sudden alteration of the amplitude of such a character as to set up a second train of smaller amplitude which in its turn was followed by an exact repetition of the first train, so that a steady succession of alternating trains was produced. No opportunity has presented itself of following this matter up, but the possibility of such a phenomenon producing an effect of frequency sub-multiplication constitutes an argument of caution as regards the use of a form of control operative in the anode circuit of a ticking oscillator, unless the nature of the impedance is such that the effect mentioned cannot take place.

AUTHOR'S reply. There is no doubt that such methods of synchronization have proved of high importance in simplifying the observational technique of ionospheric study, and we are still endeavouring to effect further refinements in the way of simplifying routine work and assisting both the annotation and reduction of the records.

With reference to the matter raised by Mr Willans, I can visualize the possibility of the action he suggests, especially in the case of the circuit which I know he was using. I feel sure, however, that the particular effect reported in the paper was definitely due to inequality of the rectified half-waves. I proved this to my complete satisfaction at the time by the use of resistance with which it was possible gradually to reduce and balance the inequality, and then, by continuing the addition of resistance, to introduce inequality in the opposite direction. It was possible, of course, to check this process in its various stages, while it was significant that the effect disappeared completely when, instead of rectified half-waves from a full-wave rectifier, unrectified a.c. was used, the valve operating on the positive half-waves as described later in the paper.

I should apologize for a drawing-error in figure 3 (*b*), which does not correctly show the 120° displacement due to successive phases of a 3-phase supply. It is, however, indicative of the manner in which the received pulse can be located at a suitable position along the time-stroke.

551.594.11

A COMPARISON OF THE FREQUENCY-CHANGE AND GROUP-RETARDATION METHODS OF MEASURING IONIZED-LAYER EQUIVALENT HEIGHTS

By R. NAISMITH, A.M.I.E.E., Radio Research Station, Slough

Communicated by Prof. E. V. Appleton, F.R.S., September 20, 1932.
Read December 2, 1932.

ABSTRACT. The paper describes a number of experiments designed to test the measurement of the equivalent heights of the ionized layers by the frequency-change and group-retardation methods. Measurements are conducted under as varied conditions as possible. The results appear to confirm the theoretical investigation recorded by Appleton in 1928. The apparatus used to measure the amount of the frequency change employed in the measurements is described.

§ 1. INTRODUCTION

Within the last decade a number of different methods have been proposed to determine the height of the ionized regions of the upper atmosphere. Some of these methods have proved more successful than others, with the result that in the more recent work on the study of these regions the two methods which form the title of this paper have been most widely used. The first, known as the frequency-change method, was used by Appleton and Barnett* in their original experimental proof of the existence of the ionized layer and has formed the basis of much later work in this country. With balanced antenna systems this method has been used successfully to study polarization and other phenomena, which up to the present has not been possible by the group-retardation method. In the application of this first method, the frequency of an emitting station is altered continuously through a small range and the interference maxima are noted at a distant receiving station. Such interference takes place between the waves which have travelled along the ground and those which have travelled through the upper atmosphere. In the second method, known as the group-retardation method, and due to Breit and Tuve†, the emitting station sends out short pulses of radio-frequency energy and the time interval is measured between the arrival of the pulse via the ground and that via the atmosphere. At first sight it would appear that these two types of measurement are not concerned with the same quantities, since in one case interference phenomena are in question and in the other group-time measurements. Until quite recently this possible difference was emphasized by the fact that widely different interpretations had been placed on the results obtained by the frequency-change method in this country and by American workers using the group-retardation method.

---

* *Nature*, p. 333 (March 1925) and *Proc. R. S.* A, **109**, 621 (1925).

† *Phys. Rev.* **28**, 568 (1926).

§2. OBJECT OF EXPERIMENT

In 1928, however, it was shown theoretically by Appleton* that, for the circumstances under which the experiments are at present carried out in this country, the two methods should give the same result. This equivalence can be illustrated in the following way.

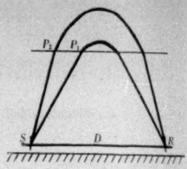


Figure 1.

D P_1 f_1, P_2 f_2 n

Consider a case of transmission from S to R. Let $SR = D$ and let P_1 be the optical path of the wave-track of the atmospheric waves when the frequency is f_1 while P_2 is the corresponding wave track when the frequency is f_2 (note that P_1 and P_2 are not identical if the refracting medium, as in this case, is dispersive). If interference fringes are produced at R there will be experienced n signal maxima (or minima) if the frequency is changed continuously from f_1 to f_2, where

$$n = \frac{1}{c}\{(P_1 - D) f_1 - (P_2 - D) f_2\} \qquad \text{......(1)}$$

c

and c is the velocity of radiation in free space. This formula is valid when the change of frequency $(f_1 - f_2)$ is large. Under the conditions of the experiment, however, the change of frequency is small and we can write in differential notation

$$\frac{\Delta n}{\Delta f} = \frac{1}{c}\left\{(P - D) + f\frac{dP}{df}\right\} \qquad \text{......(2),}$$

or

$$\left(c\frac{\Delta n}{\Delta f} + D\right) = P + f\frac{dP}{df} \qquad \text{......(3),}$$

P

where P now refers to the optical path of the mean wave-length used. The quantity $(P + f\, dP/df)$ Appleton calls the "equivalent path" of the atmospheric waves.

t

In the group-retardation method it is clear that, if t is the difference in the times of arrival of a certain pulse via the ground and via the upper atmosphere, we have

$$t = \int\frac{ds}{U} - \frac{D}{c} \qquad \text{......(4),}$$

ds

where U is the group velocity of the atmospheric waves along an element of atmospheric ray track ds and the integration extends along the whole length of this track. We then have

$$ct + D = C\int\frac{ds}{U} \qquad \text{......(5).}$$

Now Appleton, using the principle of least time as interpreted by Hamilton, has demonstrated the equivalence of the right-hand sides of (3) and (5) so that the quantity $\Delta n/\Delta f$ measured in the frequency-change method should be equal to t measured by the group-retardation method. If these quantities are shown to be equal, the equivalent paths of the atmospheric rays and therefore the equivalent heights of the deviating layer deduced from them should be the same.

---

* *Proc. Phys. Soc.* **41**, 43 (1928).

The object of the experiments described below was to see how far this suggested theoretical equivalence was borne out in practice when both methods were carried out under identical conditions.

§3. EXPERIMENTAL PROCEDURE

In the frequency-change method it is necessary to know both the amount of variation of frequency and the number of maxima and minima caused by that change of frequency. It is desirable that both these determinations should be made at the receiving station. The scheme now adopted is to set the amount of frequency change to approximately 16 kc./sec. and to measure the change accurately by a method which is described at length at the end of this paper. The signal maxima and minima were recorded on an Einthoven galvanometer with camera attachment. Preliminary experiments with a special form of syphon recorder show that it will eventually be possible to obtain these variations in signal strength directly on a tape and without the necessity for photographic equipment. With these modifications, the apparatus necessary for the experimental determination of the height of either the E or the F ionized regions of the upper atmosphere by the frequency-change method is now comparatively simple, robust and direct reading.

The pulses required for the group-retardation experiment were produced similarly to the manner described by Appleton and Builder in January 1932*. These pulses were observed on a cathode-ray oscillograph after suitable amplification. When it was desired to obtain a record of any observed pattern the photographic recording was done on a Duddell high-frequency oscillograph. One element of this oscillograph was coupled to a 1 kc./sec. oscillator which could readily be calibrated against a 1 kc./sec. tuning-fork. A second element of the oscillograph recorded the pulses due to the signal coming over the ground and the echoes present. In this way it was possible to compare directly the time interval between the initial pulse and the succeeding echoes with a 1 kc./sec. oscillator, and thus obtain the path difference between the pulse which had travelled by the upper regions of the atmosphere and that which had travelled directly over the surface of the ground from the transmitter to the receiver.

In the individual experiments quoted below a standard system of transmission was adopted. First of all a determination of the effective height of the ionized layer was made by the frequency-change method. This was followed immediately by a determination by the group-retardation method and finally by another determination by the frequency-change method. In this way it was possible to eliminate any possibility of sudden changes in the effective height at which reflection took place. The transmitter, except where the contrary is stated, was situated at the National Physical Laboratory at Teddington, and the receiver at Slough. This represents a ground distance of 18 km. The accuracy of the frequency-change measurement is estimated to be within 1 per cent, but on the group-retardation method it may not be greater than 2 per cent or even 3 per cent where measurements are made on the lower ionized region.

---

* *Proc. Phys. Soc.* **44**, 76 (1932).

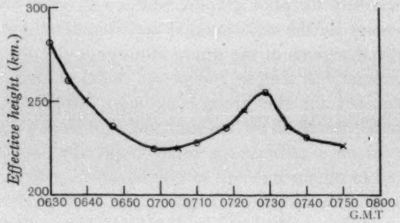
§4. EXPERIMENTAL RESULTS

The first experiment was a straightforward comparison on 85 m. It was repeated at intervals throughout the winter and table 1 gives a summary of the results obtained.

Table 1

Date	G.m.t.	Height (km.) measured by	
		Frequency change	Group retardation
30. x. 1931	12.30	253	251
3. xii. 1931	12.30	218	224
25. ii. 1932	12.00	220·5	223
7. iv. 1932	12.30	235	233

Many more observations have been made on this wave-length, but these results still represent typical values. In no case was the discrepancy greater than 2 per cent.



× Heights measured by group-retardation method } 26. 2. 32.
⊙ ,, ,, ,, frequency-change ,, }

Figure 2.

The second experiment was made on February 26, 1932, over the sunrise period in order that comparisons might be made at a time when the effective height of the ionized region was changing steadily. These results are best shown in the form of a graph (see figure 2). The same wave-length of 150 m. was used throughout the test. At 08.00 G.m.t. it was not possible to make a determination of the height owing to the fact that the density in the lower layer had increased sufficiently to cause this wave-length to be about the critical one. At 08.30 this wave-length ceased to penetrate the lower ionized region and was reflected from a height of 119 km.

The third experiment was arranged to make a comparison of the methods using the lower layer as a basis. The wave-length chosen was 150 m. and table 2 gives an example of the results obtained.

Table 2

Date	G.m.t.	Height (km.) measured by	
		Frequency change	Group retardation
25. ii. 1932	11.15	131	128
11. iii. 1932	9.15	107	108
7. iv. 1932	11.15	108	108

On April 14, 1932, the density of the *E* layer was abnormally high. This provided an opportunity to make a comparison of the methods on a very much shorter wave-length than had hitherto been possible with the *E* layer as the basis of comparison.

On 85 m. the heights measured at 12.45 G.m.t. were as follows:

Frequency change	101·5 km.
Group retardation	102 km.

An experiment on January 8, 1932, between Windsor and Slough over a ground distance of 5 km. determined the lowest wave-length which was reflected from the *F* layer. The result of this experiment showed that radiation of wave-length 45 m. was reflected but that of wave-length 42·5 m. was not. A comparison was then made on 45 m. and the heights measured at noon were as follows:

Frequency change	223 km.
Group retardation	226 km.

Another arrangement was tried with different transmitters and over different distances. The wave-lengths were made slightly different (90 and 88·3 m.) in order that practically simultaneous observations might be made. In one case the transmitter was installed near Windsor which is 9 km. from the receiver at Slough, and in the other at Rugby which is 111 km. distant. The effective height measured from Windsor was 211 km.; this was obtained by the frequency-change method. The path difference as determined by the Rugby transmission was 422 km., representing an effective height of 214 km. This latter was determined by the group-retardation method.

The large change in the angle of incidence on the layer in the two cases appears to have produced very little change in the depth of penetration into the layer.

§5. CONCLUSIONS

The above typical set of experiments were designed as far as possible to test the comparison of the frequency-change and group-retardation methods of measuring the effective height of the ionized regions of the upper atmosphere under a variety of conditions. Other observations which have been made at different times only serve to confirm in experimental terms the theoretical conclusion arrived at by Appleton in 1928 that the frequency-change method and the group-retardation method both measure the same quantity, namely,

$$c\int\frac{ds}{U}$$

for the atmospheric waves.

§6. ACKNOWLEDGMENTS

The work described in this paper was carried out as part of the programme of the Radio Research Board and is published by permission of the Department of Scientific and Industrial Research. Thanks are due to Professor E. V. Appleton, F.R.S., for initial suggestions in connection with this work. Thanks are also due to

Mr R. A. Watson Watt, Superintendent, for his interest in the work and for the provision of facilities for its conduct, and to other colleagues at the Radio Research Station, Slough, for assistance in the experiments.

APPENDIX

A device for the measurement of a small change of frequency

Object. The object of the device is to provide a means of measuring the small change of frequency required for the experimental determination of layer heights by the frequency-change method.

Principle. The principle of the device is to change the frequency f of the received signal to another frequency f_1 such that the amount Δf (by which f is changed) to be measured is sufficiently large compared with f_1 to be read directly from an oscillator calibrated over the range Δf and centred on frequency f_1.

Description. Figure 3 is a simple schematic arrangement of the device which is almost self-explanatory. In practice the first detector is tuned to the received signal. The wave-meter is tuned 100 kc./sec. off, providing a beat frequency of 100 kc./sec. which is applied to the grid of the second detector along with the output from the calibrated 100 kc./sec. oscillator. This gives zero beat after the second detector. When the frequency changes by the amount Δf, zero beat can again be obtained by retuning the 100 kc./sec. oscillator. The amount by which this oscillator has been retuned is then read off directly in kilocycles.

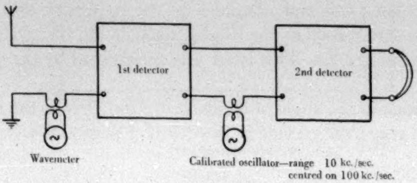


Figure 3.

Certain modifications of a very practical nature can be incorporated when the particular conditions of the experiment are known. For example when it is only desired to check a frequency change known to be approximately 16 kc./sec. a condenser can be connected by a switch across the tuned circuit of the 100 kc./sec. oscillator which will change the frequency by that amount.

All that is then necessary is to tune to zero beat and when the frequency starts changing throw the switch, and when the change of frequency stops zero beat should again be heard. If this is not so, a readjustment of the variable condenser will produce the condition and the amount of this readjustment (+ or −) will give the departure from 16 kc./sec. Other modifications (e.g. first detector oscillating and no wave-meter) can be readily incorporated but these need not be discussed here.

Advantages. No local signal of the same frequency as the received signal is present. The measurement and the photographing can therefore be done simultaneously and each individual frequency change can be measured. The time taken for the measurement, after the apparatus has been tuned to the signal, can be made as short as 3 sec. when the amount of the frequency change is known approximately. Automatic synchronization between oscillators or oscillator and transmitter is entirely absent.

The following critical test was applied. A very weak c.w. signal of 75 m. was used. The apparatus was tuned to this wavelength and the intermediate frequency oscillator adjusted until a beat note of 1 kc./sec. was heard. A low-frequency oscillator was tuned to 1 kc./sec. in the same room and the audible beats between the oscillator and incoming signal were detected by the ear. A very powerful local signal was then produced and tuned through 75 m. This signal as it passed through the tune of the high-frequency circuits did not cause the beats set up by the weak signal and the 1 kc./sec. oscillator to vary. It is considered that this test is sufficiently stringent to show that the coupling between the amplifier tuned to 100 kc./sec. and the 100 kc./sec. oscillator is sufficiently weak to eliminate any error due to this cause. The accuracy is easily within 1 per cent. A difference method is employed. This has some important advantages over systems referred to absolute standards. The most important is perhaps the simplicity of the scheme. Also any small drift from the frequency to which the oscillators are tuned is relatively unimportant. There can hardly be any ambiguity caused by beating with a harmonic instead of the fundamental.

It is possible to check whether the frequency is increasing or decreasing during any change, thus: The h.f. oscillator is tuned above the frequency of the incoming signal and the i.f. oscillator is tuned about 2 kc./sec. above the frequency to which the i.f. amplifier is tuned. The note will then rise or fall during the frequency change according to whether the change is due to an increase in the frequency of the incoming signal or to a decrease. Similar results are obtained when both oscillators are tuned below the respective frequencies.

DISCUSSION

Prof. E. V. **Appleton.** A careful comparison of results by the two available methods, such as the author has made, was very much needed and it is satisfactory to note that such good agreement has been obtained. Since we are concerned essentially with the time required for a signal to travel up to the ionosphere and back we have, as it were, to put a mark on the wave by which to recognize it. Now a wave has only two characteristics which we can control, namely frequency and amplitude. In the frequency-change method we use frequency-modulation and in the group-retardation method we use amplitude-modulation. Any other method we can devise must be a modification of the two basic ones.

Mr R. A. Watson Watt. I have already commented on the broad aspects of the author's paper in discussing the paper by Mr Herd. The good agreement shown by the experiments is, as Prof. Appleton has remarked, very satisfactory. I think the report of the experiment in which emissions from Windsor and Rugby respectively formed the material for comparison is of very special interest; it is one of many indicators towards an extended programme of comparisons between vertical-incidence phenomena on one hand and inclined-incidence phenomena on the other. It might be of interest for Mr Naismith to record whether the Rugby determination was made on ground ray and first reflection or on multiple reflections.

Mr Naismith's familiarity with the state of the general investigation may have led him to overlook the fact that two *obiter dicta* of the paper, true at the time of drafting, were no longer true at the date of communication. The group-retardation technique has for some time been used in polarization studies*, and the introduction of the syphon recorder into frequency-change working, to which we were led by a suggestion from the late Captain Lemon, R.S., was so satisfactory that the syphon recorder has been systematically used at Slough since July 1932.

Dr F. J. W. Whipple. In the introduction to this paper the author follows Prof. Appleton in considering the actual wave-tracks, and the reader who is unfamiliar with the subject may, like myself, not realize at once that the "optical path P" is merely a technical name for the product of the time of transmission of a phase and the normal velocity of light. It seems better to introduce a symbol T for the time of transmission. Then we can write down the number of waves in the path, fT, and the equation (1) of the paper becomes

$$n=(f_1T_1-f_1D/c)-(f_2T_2-f_2D/c),$$

so that (3) takes the form

$$\frac{\Delta n}{\Delta f}+\frac{D}{c}=\frac{d}{df}(fT).$$

Prof. Appleton's demonstration that the right-hand side of this equation is equal
$\mathfrak{T}$ to $\mathfrak{T}$, the time of transmission of a group, is really independent of any knowledge of the wave-tracks. We can bring this out by considering a pulse of a definite form, the initial impulse being proportional to $e^{-nt^2}\sin 2\pi f_0 t$.

By Fourier's theorem we find that

$$e^{-nt^2}\sin 2\pi f_0 t = 4\sqrt{\frac{\pi}{n}}\cdot\int_{-\infty}^{\infty} e^{-4\pi^2(f_0-f)^2/n}\sin 2\pi ft\,df,$$

so that the pulse may be regarded as the combination of trains of waves, those for which f is near to f_0 predominating.

The disturbance which reaches the receiving station is

$$4\sqrt{\frac{\pi}{n}}\cdot\int_{-\infty}^{\infty} A(f)e^{-4\pi^2(f_0-f)^2/n}\sin 2\pi f(t-T)\,df,$$

the factor $A(f)$ indicating that the attenuation of the waves may depend on frequency.

---

* *Wireless World*, July 8, 1932 and *Nature*, September 17, 1932.

The disturbance is equivalent to

$$4\sqrt{\frac{\pi}{n}}.\sin 2\pi f_0 (t - T_0)\int_{-\infty}^{\infty} A(f) e^{-4\pi^2 (f_0-f)^2/n} \cos 2\pi \{(f_0 - f)\,t - (f_0 T_0 - fT)\}\, df,$$

a similar expression with the sin and cos interchanged being neglected. The latter expression would vanish if $A(f)$ were constant.

The disturbance is a maximum when

$$(f_0 - f)\,t = f_0 T_0 - fT$$

for values of f near to f_0.

Accordingly the "group" arrives at the time t given by

$$t = \mathfrak{T} = \frac{d}{df}(fT), \quad f = f_0.$$

Obviously the result would have been the same if a different type of initial pulse had been assumed.

The author's experiments provide a beautiful verification of the identity

$$[\mathfrak{T} - D/c] = \Delta n/\Delta f.$$

It may be of interest to point out that the ordinary formula for group velocity can be deduced from the equation

$$\mathfrak{T} = \frac{d}{df}(fT),$$

by reversing Appleton's argument.

Writing U for the group velocity and V for the pulse velocity, we have

$$\int \frac{ds}{U} = \frac{d}{df}\left[f \int \frac{ds}{V}\right].$$

Now Hamilton's principle tells us that $\int ds/V$ with f constant is unaltered by slight alterations in the path of integration and therefore by the change from the path appropriate to f to that appropriate to $f + df$. Accordingly

$$\int \frac{ds}{U} = \int \frac{d}{df}\left(\frac{f}{V}\right) ds.$$

Since "group velocity" is a property of a particular set of waves and is difficult to define precisely, we cannot *prove* the formula

$$\frac{1}{U} = \frac{d}{df}\left(\frac{f}{V}\right).$$

We can say, however, that this formula is consistent with the preceding equation, and that is sufficient to justify the use of the concept, "group velocity."

AUTHOR'S reply. I am indebted to Prof. Appleton for his concise remarks. He has put the essential difference between the two methods very explicitly.

In reply to Mr Watson Watt: The comparison between the emissions from Windsor and Rugby was really done as part of another more general experiment in which I was engaged, namely the comparison of measurements on the ionosphere made over different base lines. These measurements had shown that it was possible to obtain, under certain conditions, quite different results when the base line between emitter and receiver was altered. On this particular occasion, however, the density of the *E* region was constant throughout the middle of the day when the measurements were made. The determination was facilitated by the reception of a ground pulse, and the fact that the frequency on which the comparison was made was not near the critical penetration frequency at the time.

Dr Whipple's contribution is helpful in that it presents the theoretical aspect of the subject from a different angle. This will no doubt assist certain readers to a better understanding of the problem.

621.396.11

THE APPLETON-HARTREE FORMULA AND DISPERSION CURVES FOR THE PROPAGATION OF ELECTROMAGNETIC WAVES THROUGH AN IONIZED MEDIUM IN THE PRESENCE OF AN EXTERNAL MAGNETIC FIELD

PART 1: CURVES FOR ZERO ABSORPTION

BY MARY TAYLOR, M.A., PH.D., Radio Research Station, Slough

Communicated by Mr R. A. Watson Watt, November 21, 1932.
Read December 16, 1932

ABSTRACT. This paper gives dispersion curves derived from the Appleton-Hartree formula in the case of zero absorption. The value of the magnetic field is taken as that of the earth's field at Slough. The curves are drawn to show the value of the squares of the indices of refraction and attenuation as functions of the electron density for a series of twelve frequencies, which are chosen to illustrate the various classes of curve and the boundary curves separating the classes and, in the case of frequencies above 1·321 megacycles per second, the various regions of short and ultra-short waves. The derivation and general properties of the Appleton-Hartree formula and the various possible modes of propagation are also discussed. The dispersion curves are classified according to the infinities they contain and a diagram is given to show how the classes of curve holding for any angle of inclination of the direction of propagation to the magnetic field H depend on the ratio of the longitudinal component of H to H itself. The use of the zeros and infinities of the dispersion curves in the interpretation of propagation phenomena is described and a summarizing diagram is given, showing how the possible propagation of zero, one or two basic modes for any frequency depends on the electron density. The polarization corresponding to each dispersion curve is shown graphically and the general properties of the polarizations of the basic propagation modes are discussed.

---

§ 1. INTRODUCTION

It is now well established that the presence of a magnetic field exerts considerable influence on the propagation of electromagnetic waves through a dispersive medium. The magnetic rotation of the plane of polarization was discovered by Faraday in 1845, and the Kerr and Zeeman effects in 1877 and 1896 respectively. It is to Lorentz that we chiefly owe a theoretical explanation of the phenomena on classical lines, in contradistinction to the methods of modern quantum mechanics. He assumed that the dispersion phenomena were due to the presence in the dispersive medium of discrete charged particles. An expression for the electric force acting on any one particle was found by combining the average effect of the other particles with the electric vector of the incident wave; this was used in the equations of motion of the particle (which included the effects of the external magnetic field) to get a relation between the vectorial electric force E and the vectorial dielectric

D

P_x, P_y

displacement D. Lorentz combined this relation with Maxwell's electromagnetic equations in the two simple cases of propagation (*a*) along, and (*b*) at right angles to the lines of the external magnetic force. He assumed that the external magnetic field acted along the positive direction of the axis Oz; in case (*a*) Oz was also the direction of propagation of the waves through the medium, and in case (*b*) they were propagated along Ox. Lorentz showed that in each case there were two values of the ratio of the components P_x and P_y of the vectorial polarization P, or $(D-E)$, which governed propagation through the medium*. Each of these values corresponded to a mode of propagation through the medium in which the form of the wave or vibration was unchanged, except in so far as exponential decrease of amplitude was involved; we may denote such modes by the term *basic modes*, since any other mode may be regarded as combinations of them in varying degrees. The refractive index, index of attenuation, and polarization are fixed for each mode by the value of the real or complex ratio $P_x : P_y$.

Lorentz showed that in case (*a*), when propagation was along the lines of the external magnetic force, each value of $P_x : P_y$ corresponded to a beam of circularly polarized waves, one value giving a left-handed and the other a right-handed sense of rotation of the electric vector around the positive direction of propagation of the beam. In case (*b*), with propagation at right angles to the external magnetic force, the magnetic field was found to have no influence on the electric vibrations along the lines of force, whereas waves in which the electric vector was perpendicular to the external magnetic field were in general elliptically polarized in the plane perpendicular to the external magnetic force, though they appear as linearly polarized when viewed along the direction of propagation.

The application of this theory to the explanation of phenomena in the propagation of wireless waves through the earth's atmosphere was first proposed by Appleton in 1925 (1) to account for directional errors. He drew attention to the fact that the quantity He/mc, the natural angular frequency of rotation of electrons about the earth's magnetic field, was comparable with wireless frequencies and so must be taken into account in theories of propagation. He suggested that the presence of an abnormally polarized wave giving directional errors might be due to the joint action of the ionized medium and the earth's magnetic field, which must obviously in principle affect the propagation of the waves. Since, however, the direction of propagation of the waves is seldom either along or perpendicular to the direction of the lines of force, it was necessary to extend Lorentz's treatment to the case when the magnetic field is inclined at any angle to the direction of propagation of the waves, and the formula determining the characteristics of the basic modes in this case was published by Appleton in 1927 (2). He assumed the charged centres to be free electrons, where Lorentz had regarded them as bound. The expression given by Appleton has the form

$$M^2 = \left(\mu - \frac{i\kappa c}{p}\right)^2 = 1 + \frac{2}{2(\alpha + i\beta) - \dfrac{\gamma_T^{\,2}}{1 + \alpha + i\beta} \pm \sqrt{\left(\dfrac{\gamma_T^{\,4}}{(1 + \alpha + i\beta)^2} + 4\gamma_L^{\,2}\right)}} \qquad \ldots\ldots(1).$$

---

* The Heaviside system of units, used by Lorentz, is here retained.

In this paper

c is the velocity of electromagnetic waves in vacuo; c
m the mass of an electron; m
e the charge on an electron (e.s.u.); e
N the electron-density; N
H the imposed magnetic field (gauss); H
H_L the component of magnetic field along direction of propagation; H_L
H_T the component of magnetic field perpendicular to direction of propagation; H_T
$p = 2\pi$ times the frequency of the wave considered; p
$p_0^2 = 4\pi Ne^2/m$; p_0^2
$p_H = He/mc$, and is the natural angular frequency of rotation of electrons about H; p_H
$p_L = H_L e/mc$, and is the natural angular frequency of rotation of electrons about H_L; p_L
$p_T = H_T e/mc$, and is the natural angular frequency of rotation of electrons about H_T; p_T
$\nu = 1/\tau$, and is the frequency of collision of electron with molecules; ν
$\alpha = -p^2/p_0^2 - \frac{1}{3}$; α
$\beta = p\nu/p_0^2$; β
$\gamma = pp_H/p_0^2$; γ
$\gamma_T = pp_T/p_0^2$; γ_T
$\gamma_L = pp_L/p_0^2$; γ_L
μ is the index of refraction and $= c/$(phase velocity of propagation); μ
κ is the index of attenuation; and κ
$M = \mu - i\kappa c/p$. M

The same expression, with different notation, was independently derived by Hartree (3) in his study of the general differential equations of propagation in any stratified ionized medium; he summed the waves scattered by the discrete charged centres and superposed the result on the incident plane wave. The formula (1) may therefore appropriately be called the Appleton-Hartree formula. The present paper is concerned with the dispersion curves to be derived from it and used in the interpretation of wireless reception phenomena. We may note at once that, when the external magnetic field has a non-zero value, the two values of M are only equal if (1) $N = 0$ or (2) $1 + \alpha = 0$ and $\gamma_T^4 - 4\beta^2\gamma_L^2 = 0$ simultaneously; these cases are the only ones in which the two basic modes of propagation given by the alternative signs before the square root can be the same. The theory strictly holds only when the number of electrons in a cube whose side is a vacuum wave-length is large; it is thus not to be expected that the formula will correspond rigidly to physical reality for very small values of N, but it does give $M^2 = 1$ when $N = 0$, as physical considerations demand. This point arises again later, in connexion with the dispersion curves.

In deriving the formula, absorption was regarded as caused by collision of the free electrons with the neutral molecules of the gaseous atmosphere around them. The frequency ν of these collisions per electron is a variable quantity and increases with the density of the atmosphere. The curves given in the present paper are restricted to the case $\nu = 0$; those for small values of absorption differ only slightly from those given here, though the presence of even a small amount of absorption removes the infinities on the dispersion curves, as is usual in physical theory, and also requires that μ and κ in (1) be never actually zero.

The discussion given by Goldstein (4) treated the medium as a homogeneously charged fluid, in contrast with the discrete charged centres assumed by Lorentz, Appleton and Hartree, and disregarded the effect of collisional friction which was included by the other writers named. The dispersion curves derived on this assumption may differ considerably from those given by the Appleton-Hartree formula, particularly at low frequencies.

§ 2. MODES OF PROPAGATION

In discussing the general properties of the Appleton-Hartree formula and the types of dispersion curves it gives, it is convenient to start from the form (1) in which it was derived by Appleton. The alternative signs to the square root show that M^2 has two values for any one set of values of p, N, H_L, H_T and ν, so that, generally speaking, there are two basic modes of propagation of electromagnetic vibrations of angular frequency p through a medium of constant electron-density with a given magnetic field and collision-frequency. These modes are defined and distinguished by (*a*) the two values of M^2, and (*b*) the polarizations corresponding thereto, which have been shown by Appleton and Hartree to be given by

$$-\frac{E_x}{E_y}=\frac{H_y}{H_x}=\frac{i\gamma_L(1-M^2)}{1+(\alpha+i\beta)(1-M^2)} \qquad \ldots\ldots(2),$$

where the incident wave is propagated along the positive direction of Oz and the external magnetic field has components H_L and H_T along Oz and Ox respectively.

The vibration actually occurring in the medium is determined for continuous waves by the proportion in which the modes are present at any time and may be found by the usual method of building up a wave in the medium by superposition of the possible basic vibrations. We suppose the incident wave to be travelling along the positive direction of Oz. If we distinguish the two values of M^2 by the suffixes
a, b *a* and *b* when the positive and negative signs respectively are prefixed to the square root in the denominator of the right-hand side of (1), we see, following Lorentz*, that the components of the vectors describing the electromagnetic field are represented by the real parts of expressions built up by adding the four quantities $e^{-\kappa_r z + ip(t \pm \mu_r z/c)}$ $(r = a, b)$, each multiplied by a constant factor determining its amplitude and phase. The factors are found in any actual case by connecting the total vibration to the incident wave of given polarization and amplitude by means of the boundary conditions to be satisfied at the surface of the ionized medium.

The phase velocity of propagation of a basic mode is c/μ_r, so that the index of refraction

$\boldsymbol{\mu_r}$ $$\mu_r = c/(\text{corresponding velocity of phase propagation}).$$

---

* *Theory of Electrons*, p. 153 (1916).

The quantities κ_r determine the rate at which the amplitudes of the vibrations decrease and are called by Lorentz the indices of absorption, although, as will be seen below, true absorption of energy only occurs when $\nu \neq 0$, i.e. when friction is present; in this paper κ_r is called the "index of attenuation."

κ_r

The basic modes of propagation fall into three types, which are distinguished by the nature of M_r^2 in the following way.

M_r

(i) When M_r^2 is real and positive, μ_r has a non-zero value and κ_r is zero; this corresponds to the propagation of progressive waves along the positive or negative direction of the z-axis with phase velocity c/μ_r and constant amplitude. (ii) When M_r^2 is complex, κ_r is no longer zero and the progressive waves propagated, as in (i), in the positive and negative directions of Oz suffer exponential diminution of amplitude. This falls to $1/e$ of its value in a distance κ_r^{-1}. (iii) When M_r^2 is real and negative, μ_r is zero but κ_r has a non-zero value and the vibrations of a scalar quantity y take the form

y

$$y = \cosh \kappa_r z \cos pt \mp \sinh \kappa_r z \sin pt$$

as compared with the form

$$y = \cos \kappa_r z \cos pt \mp \sin \kappa_r z \sin pt$$

of the progressive waves of (i). This is the type of disturbance which penetrates a medium where $M_r^2 < 0$. Such a medium is usually taken as totally reflecting, but, if it is finite in thickness, some penetration through it can take place, especially if its thickness is small compared with a vacuum wave-length. The limiting condition for $M_r^2 < 0$ is given by the point on the dispersion curve at which μ_r vanishes.

We note that, since actual absorption of energy can only take place when $\mu_r \kappa_r \neq 0$*, the second type of vibration is the only one in which energy is absorbed. $\mu_r \kappa_r$ is, save for the factor $2c/p$ depending on the frequency, the imaginary part of the right-hand side of (1), and cannot therefore have a non-zero value unless friction is present.

From the above discussion it is clear that, in order to predict the nature of the wave which will be propagated under any given conditions, and to discover what will happen to any wave incident on the ionized medium, we must first investigate the properties of the Appleton-Hartree formula and the types of dispersion curve given thereby. It may be well to emphasize here that the formula does not refer to media in which N is varying, but only to a uniform medium with constant N; it gives the types of vibration propagated in such a medium extending to infinity in the plane of the wave-front.

Discussion of a medium with variable N is only possible by working with the appropriate differential equations assuming the N-distribution corresponding to the medium; analytical solution of the equations in terms of known functions has not yet been performed except with a stepped N-distribution, consisting of a system of regions of finite extent in each of which N is constant. In this case the values of M_r given by the Appleton-Hartree formula may be used to build up a wave in each separate region as described above. The unknown constants in this wave are determined by satisfying the boundary conditions. The reflected wave corresponding to an incident wave of given frequency, amplitude and polarization may be determined as regards amplitude, phase and state of polarization.

---

* Cf. Drude, *Theory of Optics*, pp. 366–367.

§ 3. TYPES OF DISPERSION CURVE

The physical quantities which define the medium under discussion are the longitudinal and transverse components H_L and H_T of the imposed magnetic field, the collision-frequency ν, the angular frequency p of the waves under investigation, and the density N of the charged scattering centres, which we will henceforth assume to be electrons. With so many variables there are several possible types of dispersion curve or surface and, in deciding which shall be most fully discussed, we must consider which are likely to be of the greatest utility to those engaged in experimental researches on the propagation of waves. The chief application of the Appleton-Hartree formula is to the interpretation of the results of experiments on the electrical constitution of the ionosphere. The formula was deduced by considering the case of waves incident normally on the ionized medium, and many experiments have been and are being done by emitting waves very close to the receiver and observing the wave reflected vertically downwards by the ionosphere. For such emissions H_L and H_T are fixed by the elements of the earth's magnetic field in the region where the experiments are carried out, since the emitter and receiver are very nearly at the same place. The collision frequency ν may next be fixed; it will be zero in the absence of friction, and a set of curves with values of ν increasing from zero will show the gradually increasing effect of friction on the properties of the medium.

The only independent variables remaining when the value of ν has been fixed are the angular frequency p and the electron density N. Experiments are generally designed to send a wave of given frequency into the ionosphere, where it meets a dispersive medium of gradually increasing N; thus, if we wish to be able to interpret the constitution of the reflected wave, we must draw the dispersion curves corresponding to the experimental arrangement—that is, we must fix p and find how the two values M_r^2 vary as N gradually increases from zero. The curves will then represent the conditions actually met by the wave as it penetrates into the medium, and also those encountered by the reflected wave on its return to the receiver. A set of such curves will be sections of three-dimensional (p, N, M_r^2) surfaces; sections of the surfaces at right angles to those from which they were built up will be dispersion curves giving the variation of M_r^2 with p for constant N. The dispersion curves given in this part of the paper are restricted to those for which $\nu = 0$; curves giving the values of μ_r and κ_r for three degrees of damping of different orders of magnitude, for four typical wave-lengths, with the corresponding polarizations, will form the subject of part 2.

§ 4. CASE OF ZERO DAMPING: CLASSIFICATION OF (N, M_r^2) DISPERSION CURVES

In the case where the electrons are not subject to collisional friction, we set $\nu = 0$ and therefore $\beta = 0$ in the expression on the right-hand side of (1). Both values of M_r^2 now remain real, though they may be positive, negative or zero, and the only modes of propagation which can occur are (i) and (iii), described in § 2.

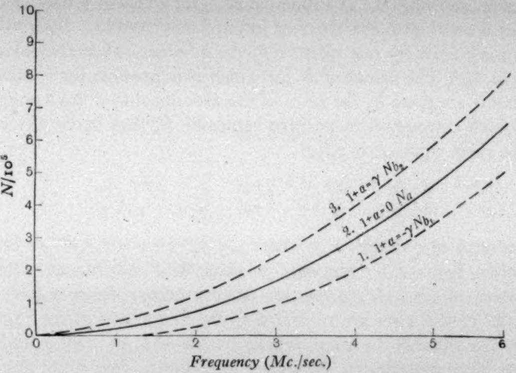


Figure 1. (Frequency, N) curves for $M_r = 0$.

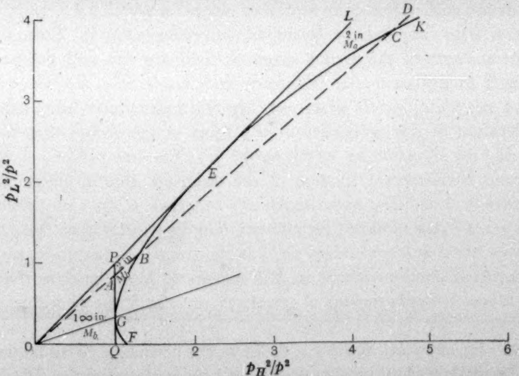


Figure 2. Ranges of magnetic field and frequency for various classes of (N, M_r^2) curves.

These modes are separated by the points, shown in figure 1, at which $M_r^2 = 0$. Discussion of the use of the curves giving $M_r^2 = 0$ is deferred until § 6, as their interpretation requires the use of the actual dispersion curves, which will now be described.

Since M_r^2 is now always real, it is convenient to represent μ_r and κ_r on one diagram, by drawing the curves for M_r^2 as functions of N, and remembering that points above the line $M_r^2 = 0$ give μ_r^2 and refer to mode (i), while points below this line give $\kappa_r^2 c^2/p^2$ and refer to mode (iii).

The curves showing M_r^2 as a function of N for constant p may be divided into four classes according to the types of infinity they contain. Both values of M_r^2 never become infinite for one value of p; the infinities, when they exist, lie either in M_a^2 or in M_b^2. The values of N for which it is possible for a value of M_r^2 to become infinite are given by the zeros of the denominator of the Appleton-Hartree formula, which correspond to positive values of N, that is, by the real positive roots of the cubic equation in p_0^2/p^2:

$$\left(\frac{p_0^2}{p^2}\right)^3 + \frac{9}{2}\left(\frac{p_0^2}{p^2}\right)^2 + \frac{27}{2}\left(\frac{p_0^2}{p^2}\right)\left(\frac{p_H^2}{3p^2} - \frac{p_L^2}{p^2}\right) + \frac{27}{2}\left(\frac{p_H^2}{p^2} - 1\right) = 0 \quad \ldots\ldots(3).$$

Taking Cartesian co-ordinates x, y where $x = p_H^2/p^2$, $y = p_L^2/p^2$, we can represent in one diagram, figure 2, the ranges of magnetic field and frequency for which the various classes of (N, M_r^2) dispersion curves occur. Since p_H^2/p^2 and p_L^2/p^2 both > 0 and $p_L < p_H$, we are restricted to the first octant of the (p_H^2/p^2, p_L^2/p^2) plane. Any line through the origin defines a value of p_L/p_H, that is, of the angle of dip, so that when considering the curves applying to any given place we move along one particular straight line through O; the angular frequency p is infinite at the origin and decreases as we move outwards. At Slough (latitude 51½° N., longitude 0°30′ W.) we are on the line OD; it is with reference to this line that the curves shown have been drawn and, as it is quite typical of places for which $p_L^2 > \frac{1}{3}p_H^2$, the general phenomena will for simplicity be described with reference to it. From the absolute value of the strength of the earth's magnetic field, we can find the point on OD corresponding to any particular frequency and, conversely, the frequency corresponding to any point on OD which we may find particularly interesting.

Consideration of the properties of the roots of (3) shows that there is one infinity in M_b^2 for all points for which $p_H^2/p^2 < 1$. The line $p_H^2/p^2 = 1$ corresponds to the natural frequency of rotation of the electrons around the total magnetic field and gives at A on OD a wave-length 227·1 metres. Class 1 of dispersion curve (see figure 3·1, 1–5) is obtained for all wave-lengths shorter than this; the infinity in M_b^2 moves towards larger values of N as the frequency increases and dM_b^2/dN always < 0. At A another infinity in M_b^2 appears at $N = 0$ and, as the frequency decreases, moves towards regions of greater N until at B the two infinities in M_b^2 coincide.

The curve for 227·1 m., figure 3·1, 6, shows the boundary curve between classes 1 and 2. The mathematical infinity appearing here at the origin in M_b^2 has no real physical meaning; the theory giving the Appleton-Hartree formula is based on the assumption that a large number of electrons is contained in a cube of the medium whose side is one vacuum wave-length, so that it does not strictly apply in the immediate neighbourhood of $N = 0$. The dispersion curves must all start from $M_r^2 = 1$ for $N = 0$; exact investigation of physical behaviour in the neighbourhood

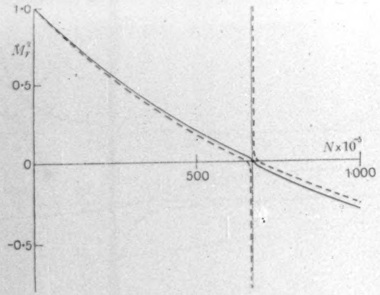


Figure 3·1, 1. $\lambda = 5$ metres.

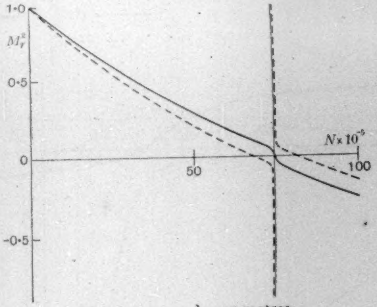


Figure 3·1, 2. $\lambda = 15$ metres.

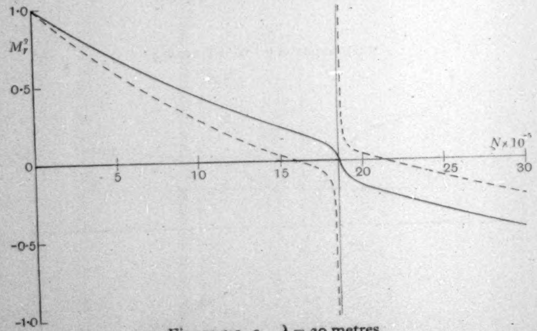


Figure 3·1, 3. $\lambda = 30$ metres.

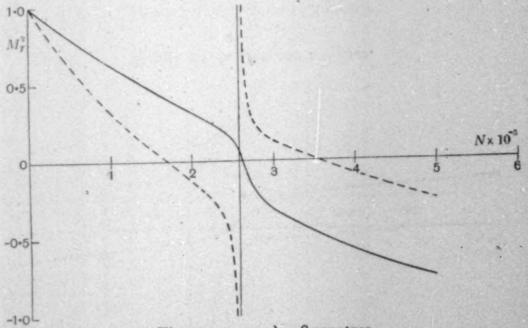


Figure 3·1, 4. $\lambda = 80$ metres.

Figures 3·1, 1 to 3·1, 4. (N, M_r^2) curves. M_a^2 ——— M_b^2 - - - - - -

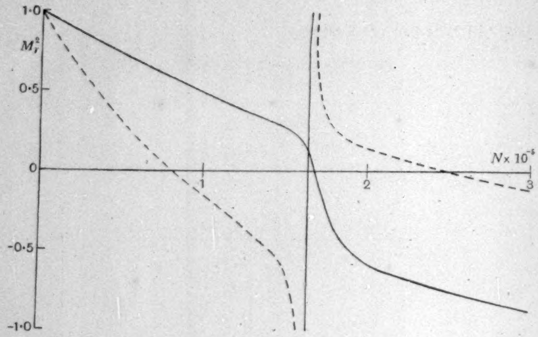


Figure 3·1, 5. $\lambda = 100$ metres.

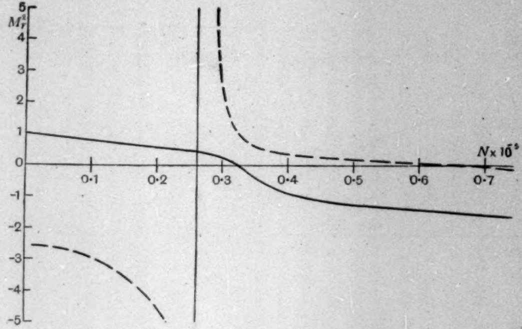


Figure 3·1, 6. $\lambda = 227·1$ metres.

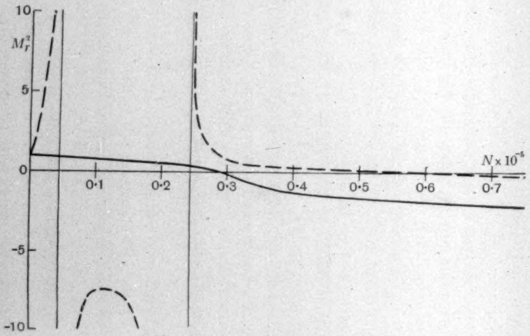


Figure 3·1, 7. $\lambda = 240$ metres.

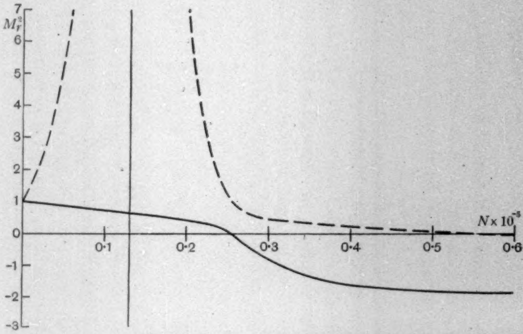


Figure 3·1, 8. $\lambda = 256·2$ metres.

Figures 3·1, 5 to 3·1, 8. (N, M_r^2) curves. M_a^2 ——— M_b^2 - - - - - -

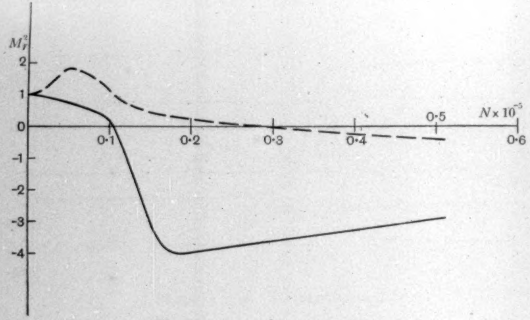


Figure 3·1, 9. $\lambda = 400$ metres.

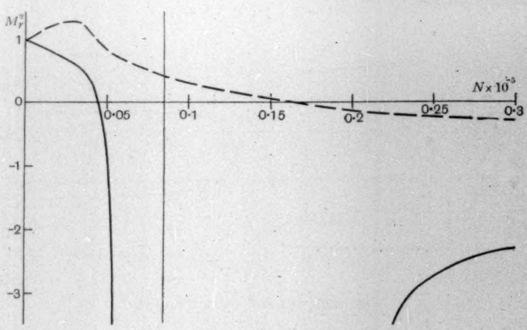


Figure 3·1, 10. $\lambda = 615{\cdot}5$ metres.

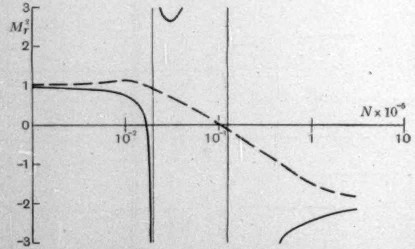


Figure 3·1, 11. $\lambda = 1000$ metres.

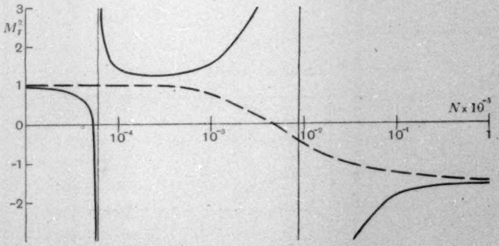


Figure 3·1, 12. $\lambda = 18{,}000$ metres.

Figures 3·1, 9 to 3·1, 12. (N, M_r^2) curves. M_a^2 ——— M_b^2 - - - - - -

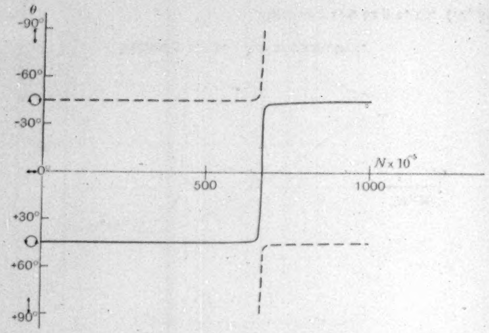


Figure 3·2, 1. λ = 5 metres.

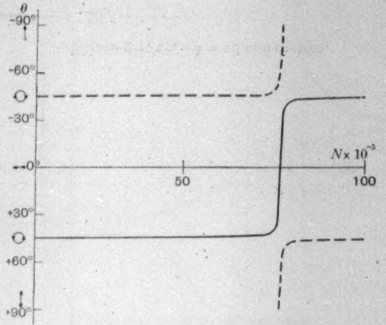


Figure 3·2, 2. λ = 15 metres.

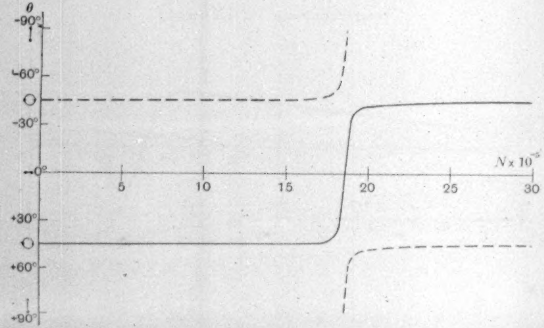


Figure 3·2, 3. λ = 30 metres.

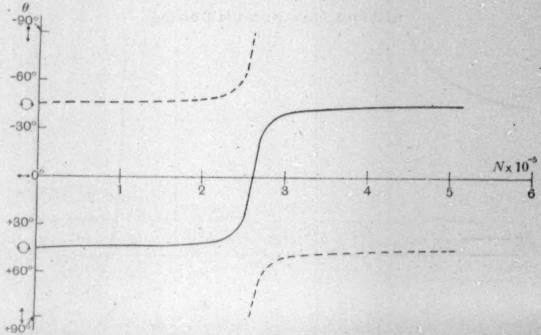


Figure 3·2, 4. λ = 80 metres.

Figures 3·2, 1 to 3·2, 4. Polarization curves. M_a^2 ———— M_b^2 - - - - - -

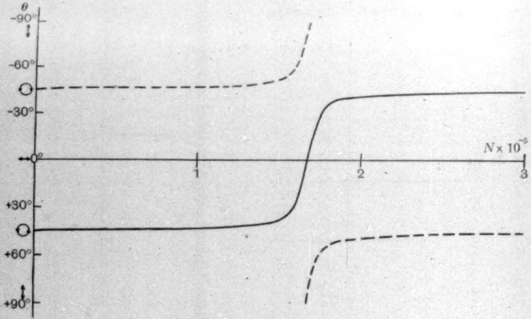


Figure 3·2, 5. $\lambda = 100$ metres.

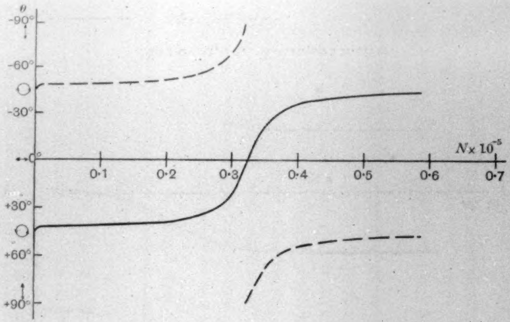


Figure 3·2, 6. $\lambda = 227{\cdot}1$ metres.

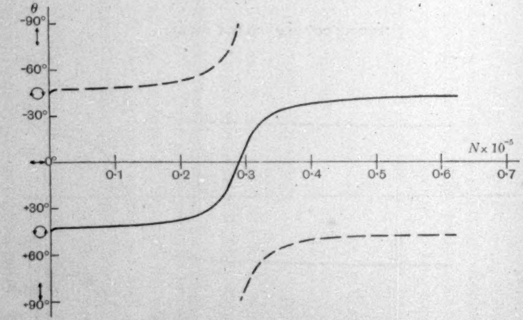


Figure 3·2, 7. $\lambda = 240$ metres.

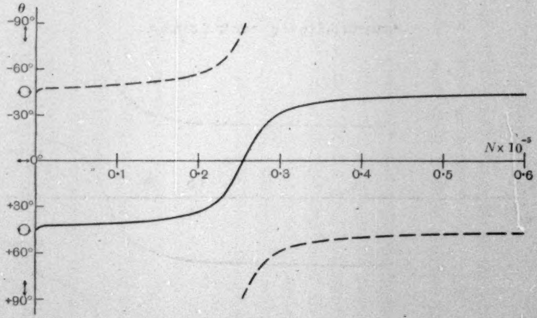


Figure 3·2, 8. $\lambda = 256{\cdot}2$ metres.

Figures 3·2, 5 to 3·2, 8. Polarization curves. M_a^2 ——— M_b^2 ------

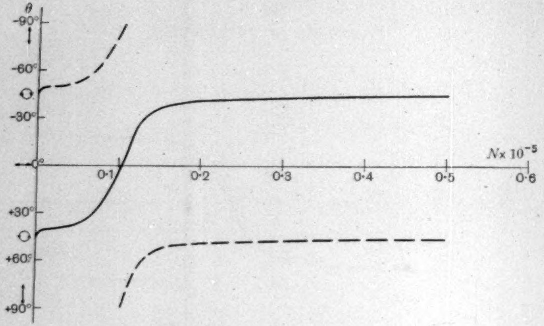


Figure 3·2, 9. $\lambda = 400$ metres.

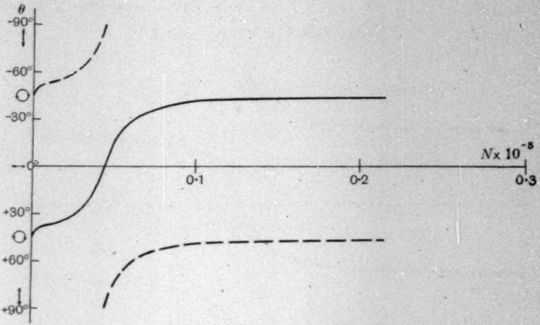


Figure 3·2, 10. $\lambda = 615{\cdot}5$ metres.

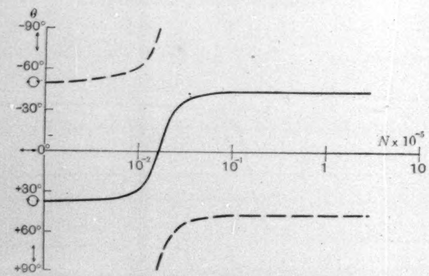


Figure 3·2, 11. $\lambda = 1000$ metres.

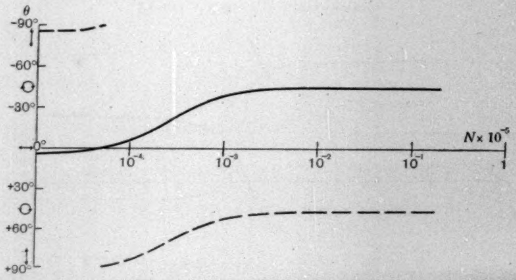


Figure 3·2, 12. $\lambda = 18{,}000$ metres.

Figures 3·2, 9 to 3·2, 12. Polarization curves. M_a^2 ——— M_b^2 - - - - - -

of $N=0$ would require examination of the validity near this point of the fundamental assumptions of the theory, and falls outside the scope of this paper. The M_b^2 curve for $\lambda = 227\cdot 1$ m. has been drawn starting at a finite distance from $N=0$.

This difficulty that the curve for $p = p_H$ gives $M_b^2 \to -\infty$ in the limit for $N \to 0$ is not peculiar to the problem of propagation of electromagnetic waves in an ionized medium in the presence of an external magnetic field but occurs at resonance in any dispersion problem, e.g. in the case of classical oscillators. In the Lorentz form of dispersion theory, the value $M^2 = \infty$ at resonance occurs however few the oscillators, and one gets $M^2 \to \infty$ as $N \to 0$, though, putting first $N=0$ and then $p \to$ resonance frequency, one gets $M^2 = 1$. Care is thus necessary in inversion of limits, since in our problem we have

$$\lim_{N\to 0} \lim_{p\to p_H} M_b^2 \neq \lim_{p\to p_H} \lim_{N\to 0} M_b^2.$$

In the present case it is the second-order terms involving the magnetic field which prevent M_b^2 having an infinite value for all N at this frequency.

The introduction of even a small amount of friction causes the infinity to disappear, just as in the ordinary Lorentz dispersion formulae.

The curve for 240 m., figure 3·1, 7, is given as an illustration of class 2, with two infinities in M_b^2. The curve for 256·2 m., figure 3·1, 8, is the boundary between classes 2 and 3; $M_b^2 \to +\infty$ on both sides of the value of N for which it becomes infinite. Between B and C neither M_a^2 nor M_b^2 has any infinities, since equation (3) has no real positive roots. This class 3 is illustrated by the curve for $\lambda = 400$ m., figure 3·1, 9. At C, corresponding to $\lambda = 615\cdot 5$ m., figure 3·1, 10, for which the curve is shown, a double infinity appears in M_a^2 and for lower frequencies this separates into two, one of which moves towards very small values of N. This class 4 is illustrated by the curves for $\lambda = 1000$ m. and $\lambda = 18{,}000$ m., figure 3·1, 11 and 12.

The curve in the (x, y) plane which separates the regions of two and zero infinities is the cubic curve *FGBECK*, whose equation is

$$8\left(\tfrac{1}{3}x - y\right)^3 - \tfrac{1}{3}x^2 + 14xy - 3y^2 - 12y = 0 \qquad \text{......(4).}$$

It is tangential to $x=1$ at G, where $y=\frac{1}{3}$, and to the line $y=x$ at E, where $x=y=\frac{9}{4}$. In the whole of the region *OPQ* there is one infinity in M_b^2; in *GPE* there are two infinities in M_b^2, and in *LEK* two in M_a^2. Within the whole of the region lying between *QGBECK* and the line $x=0$ there are no infinities in either M_a^2 or M_b^2. Thus at places, such as those near the magnetic equator, for which $p_L^2 < \frac{1}{3}p_H^2$, there are only two classes of (N, M_r^2) dispersion curves, one with one infinity in M_a^2 and the other with no infinities in either M_a^2 or M_b^2. These are the Slough classes 1 and 3; see, for instance, figure 3·1, 4 and 9. At places where p_L^2 lies between $\frac{1}{3}p_H^2$ and p_H^2, there are the four classes of curve described above with reference to the line *OD*. Thus figure 2 enables us at once to determine the type of dispersion curve holding for any given frequency at any given place.

For the line *OD* the point *B* corresponds to $\lambda = 256{\cdot}2$ m. and *C* to $\lambda = 615{\cdot}5$ m. That these values coincide very nearly with p_L and p_T, the natural frequencies of rotation about the longitudinal and transverse components of the magnetic field respectively, is seen from figure 2 to be due to the value of the angle of dip at Slough rather than to any deeper physical cause. The cubic curve represented by equation (4) seems to have no simple physical significance.

§5. NOTES ON THE DISPERSION CURVES ILLUSTRATED

(N, M_r^2) dispersion curves for vertical reflection from the ionosphere at Slough are given in figure 3·1 for the wave-lengths shown in the figure. They fall into the following classes: Class 1, one infinity in M_b^2, figures 3·1, 1 to 3·1, 5. Boundary curve, figure 3·1, 6. Class 2, two infinities in M_b^2, figure 3·1, 7. Boundary curve, figure 3·1, 8. Class 3, no infinities, figure 3·1, 9. Boundary curve, figure 3·1, 10. Class 4, two infinities in M_a^2, figures 3·1, 11 and 3·1, 12.

Apart from the boundary curves between the classes, the wave-lengths illustrated have been chosen with a view to demonstrating the effect of the presence of a magnetic field on propagation at the various ranges of frequency which are roughly divided off by the experience of practical wireless transmission. It is hoped that the curves may prove to be of practical value to those engaged in experiments on the nature of radio propagation. Each curve has been treated on its own merits and a scale has been chosen for it which will bring out its peculiar properties (e.g. the points where $M_r^2 = 0$, the various branches and asymptotes) as clearly as possible. The *N* and M_r^2 scales are therefore not uniform throughout the set; the *N* scale in particular becomes very much more spread out as the frequency decreases. For the long-wave-length curves of class 4 it was necessary to choose a logarithmic scale in order to show the behaviour for small values of *N*.

The effect of the magnetic field does not begin to be noticeable for the values of *N*, greater than 10^6, which are believed to exist in the ionosphere, until the wave-length *in vacuo* has increased from zero to the order of 30 m., figure 3·1, 3. For longer wave-lengths the effect becomes stronger, and for $\lambda = 80$ and 100 m., figures 3·1, 4 and 5, the dispersion is very marked from $N = 0{\cdot}5 \times 10^5$ to $N = 4 \times 10^5$, so that the magnetic field may be expected to have a large influence on propagation in this region. As λ increases, the range of *N* in which the effect of the magnetic field is important moves towards smaller values.

§6. USE OF THE ZEROS AND INFINITIES OF THE DISPERSION CURVES IN THE INTERPRETATION OF PROPAGATION PHENOMENA

Appleton and Hartree have shown that the points where $M_r^2 = 0$ are determined by

$$\left.\begin{aligned} 1 + \alpha &= 0 \text{ for } M_a^2 \\ 1 + \alpha &= \pm\gamma \text{ for } M_b^2 \end{aligned}\right\} \qquad \text{......(5)},$$

i.e.

$$\left.\begin{aligned} p_0^2 &= \frac{3}{2}p^2 \quad \text{for } M_a^2 \\ \frac{2}{3} - \frac{p^2}{p_0^2} &= \pm\frac{pp_H}{p_0^2} \text{ for } M_b^2 \end{aligned}\right\} \quad \ldots\ldots(5\,a).$$

We notice that $M_b^2 = 1$ for $M_a^2 = 0$, when $N = N_a$, say.

Since $p_0^2 = 4\pi Ne^2/m$, these equations give the critical values of N for which $M_r^2 = 0$ at any given frequency. They are shown in figure 1 as functions of the frequency.

Curve 2, figure 1, shows N_a, the value corresponding to $M_a^2 = 0$, which is independent of the magnetic field and exists for all frequencies; N_b, corresponding to $M_b^2 = 0$, has two values: N_{b_1} shown in curve 1, figure 1, corresponding to the equation $1 + \alpha = -\gamma$, and N_{b_2}, shown in curve 3, figure 1, corresponding to the equation $1 + \alpha = +\gamma$. For $p < p_H$ there are no values of N_{b_1}. In considering which of the curves in figure 1 is likely to give a point of reflection, we must also consult the actual dispersion curves given in figure 3·1.

From these we see that, for all angular frequencies greater than p_H, i.e. for all wave-lengths less than 227·1 m. (determined by the value of the earth's magnetic field prevailing at Slough) the wave corresponding to M_a^2 (frequently called the "ordinary wave") may be expected to be reflected by values of N given by N_a, while that corresponding to M_b^2 (frequently called "extraordinary wave") may be expected to be reflected by N_{b_1} as it goes up to meet increasing values of N. The disturbance beyond N_{b_1} produced by the wave reflected there will in general have diminished so much in amplitude before it meets densities at which its propagation is again of type (i), § 2 (between the infinity line and N_{b_2}) that no appreciable amount of energy remains to be reflected by N_{b_2}. We may therefore expect the extraordinary wave to be reflected before the ordinary wave at these frequencies, and so to have a shorter delay-time when the reflection of pulses is being studied. If, however, the variation of N is so rapid that the disturbance is still appreciable when N attains the value N_{b_2}, it would be reflected there but would probably not have sufficient amplitude after reflection and attenuation to cause an appreciable disturbance in the region $N < N_a$ on the return journey. There is, however, the theoretical possibility that it might do so and be reflected as an echo of very long delay.

For longer wave-lengths the phenomena become more complicated. At frequencies belonging to class 2, for instance $\lambda = 240$ m., figure 3·1, 7, there is a possibility of reflection of the extraordinary wave before either of the zeros N_a or N_{b_2} is reached, owing to the early occurrence of the first infinity in M_b^2. The ordinary wave will still be reflected from its zero at N_a, but a rapid increase in N will be required to enable the extraordinary wave disturbance to pass through to N_{b_2} and be reflected there. At the boundary between classes 2 and 3, where $\lambda = 256{\cdot}2$ m., the total reflection for both the ordinary and extraordinary waves occurs at the zeros of M_r^2, but now the curves to use in figure 1 are 2 and 3 instead of 1 and 2 as they were in class 1; we should now expect the ordinary wave to give the reflected pulses of lesser delay. We may here notice that $M_b{}^2 > 1$ for values of N up to N_a in curves of type 3 means simply that the phase velocity of propagation of the extraordinary wave is less than the velocity of light for such values of N; this holds for any N where $M_b{}^2 > 1$. This behaviour is typical also of class 3 and the boundary curve between classes 3 and 4. With class 4 there is in addition the possibility that the ordinary wave disturbance may pass through the very small variation in N required to make its propagation possible again. On these long wave-lengths it seems quite probable that transmission of the ordinary wave may take place through its first totally reflecting region; it would then be reflected from its second infinity point as a long-delay echo. The behaviour of $M_b{}^2$ is regular in this case; it is simply totally reflected from N_{b_2}.

The values of N which are required to reflect waves of class 4 are, however, so small that the absorption must be very large in the region where they are reflected; this will probably have the effect of smoothing out the infinities and bumps on the curves, so that the small regions of possible propagation near the asymptotes are practically eliminated. For these long wave-lengths there may be a true discontinuity and an effective sharp boundary to the reflecting layer, since continuity of N physically means a small change in a wave-length.

§ 7. (p, N) REGIONS OF PROGRESSIVE PROPAGATION OF THE BASIC MODES

The complicated reflection phenomena described in the preceding paragraph are summarized in figure 4, which shows the division of the (p, N) plane into

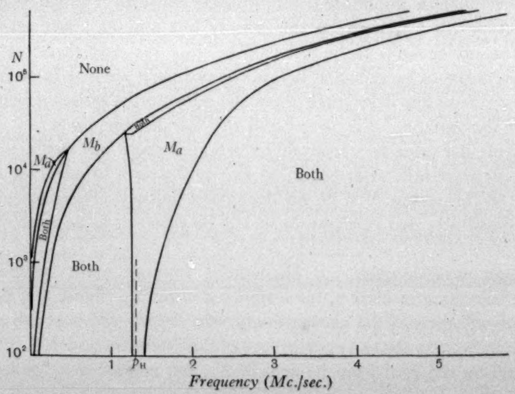


Figure 4. Division of (p, N) plane into regions of progressive propagation of the basic modes.

regions of progressive propagation of the basic modes, i.e. regions which give type (i), § 2, for one or other of the modes. A logarithmic N scale spreads out the curves for small p and N which are all asymptotic to the N-axis; in drawing the curves in this region, it was thought important to stress their relative positions rather than to adhere closely to the calculated values. A line drawn parallel to the N-axis for any given frequency will show the successive propagation conditions encountered by upgoing waves of that frequency; in using the diagram it should be remembered that, with a sufficiently large variation of N within a wave-length, it may be possible for the wave disturbance to pass through the totally reflecting region into a region where it can be propagated again, and to suffer reflection at the upper boundary and perhaps further reflection back and forth until it emerges after a long delay or is too attenuated to be detected.

§ 8. POLARIZATION

Equation (2) determines the polarizations corresponding to the two values of M_r^2. Those corresponding to the (N, M_r^2) curves of figure 3·1 are shown graphically in figures 3·2, 1 to 3·2, 12. The angle θ which is shown as a function of the electron-density is defined by the equation

$$\tan\theta = iEy/Ex = Hx/iHy,$$

where the axes Ox and Oy are respectively along and perpendicular to the transverse component of the earth's magnetic field; $\tan\theta$ thus gives the ratio of the axes of the ellipse described by the electric vector in the (x, y) plane. Linear polarization along Ox is given by $\theta = 0$ and along Oy by $\theta = \pm 90°$; positive values of θ correspond to an anticlockwise (left-hand) direction of rotation viewed along the direction of propagation, and negative values of θ to clockwise (right-hand) rotation*. $\theta = 45°$ corresponds to left-hand circular and $\theta = -45°$ to right-hand circular polarization. For values of θ between 0° and $\pm 45°$ the ellipse has its major axis along Ox, for values of θ between $\pm 45°$ and $\pm 90°$ along Oy. We note that there is a possible ambiguity of θ with respect to whole multiples of 180°.

In every case the limiting polarizations corresponding to M_a^2 and M_b^2 as $\mathrm{N} \rightarrow 0$ are circular and are left-handed and right-handed respectively, when the positive direction of H_z is along the positive direction of propagation of the mode considered†. These are the conditions which apply to the down-coming waves in the northern magnetic hemisphere. The diagrams show that as N increases the polarizations remain very nearly circular until the wave reaches the immediate neighbourhood of the point N_a where $M_a^2 = 0$, $M_b^2 = 1$. Then they rapidly become elliptical; the y-axes of the ellipses corresponding to M_a^2 and M_b^2 become relatively smaller and greater respectively, until at the point $N = N_a$ the polarizations are linear, along the x- and y-axes respectively. For greater values of N they open out and soon become nearly circular again. The polarization corresponding to M_a at the points N_{b_1}, N_{b_2}, where $M_b^2 = 0$, is given by $Hy/Hx = \pm i\gamma_L/\gamma$ respectively, so that θ is a function of the angle of dip alone.

---

* Note that in figures 3·2, 1–12 the positive values of θ are below the N-axis.

† The charge on an electron, the sign of which determines that of γ_L, is negative.

In the present case of zero absorption, the principal axes of the ellipse remain along the x- and y-axes. The axes are the same for the two waves and the direction of description is opposite in the two cases. Their ellipticities are the same, but the major axis of the one is the minor axis of the other. Mathematically speaking, the product of the polarizations at any point is -1 and the two values of θ are complementary in magnitude. The main effect of friction on polarization is to rotate the principal axes through an angle which may be calculated for any point; the product of the polarizations is still, however, -1. This subject will be discussed in Part II.

§9. ACKNOWLEDGMENTS

This work was carried out at the Radio Research Station, Slough, as part of the programme of the Radio Research Board of the Department of Scientific and Industrial Research, and is published by permission of the Board. Thanks are due to Mr R. A. Watson Watt, Superintendent of the Station, for his interest in the work and for the provision of facilities for its conduct; to Prof. E. V. Appleton and Prof. D. R. Hartree for valuable discussion, and suggestions as to the presentation of the paper; to Miss A. C. Stickland for assistance in the calculations, and to Mr E. C. Slow for help in drawing out the curves.

REFERENCES

(1) E. V. Appleton. *Proc. Phys. Soc.* **37**, 16 D (1925).
(2) E. V. Appleton. *U. R. S. I. papers* (Washington 1927).
(3) D. R. Hartree. *Proc. Camb. Phil. Soc.* **27**, 143 (1931).
(4) S. Goldstein. *Proc. R. S.* A **121**, 260 (1928).

DISCUSSION

Mr R. A. Watson Watt. The author's interim report of progress in her heroic investigation of the theory of propagation of electromagnetic waves in an ionized medium under an external magnetic field is timely and valuable. I was, some years ago, so strongly impressed by the need for such a general investigation and by the formidable difficulties of bringing together adequate mathematical and physical skill and adequate computing facilities for bringing the problem to numerical solution that I suggested to the Radio Research Board that the work should be taken up at Slough, where close contact with experimental work would be a valuable guide to the mathematical investigator.

The results now presented, despite the limitations arising from neglect of collisional damping, are of a kind required by all investigators concerned with the mechanism of return of wireless waves from the ionosphere, and this paper will stand as a source from which initial data for new investigations can be obtained without duplication of effort.

It is satisfactory that we can report that the investigation of typical cases, taking account of collisional damping, is making satisfactory progress and may be reported at a comparatively early date.

Prof. E. V. Appleton. All experimental workers in the field of ionospheric investigations will welcome Dr Taylor's exhaustive representation of illustrative magneto-ionic dispersion curves. It is only by having the theory so fully worked out for us at the first stage that we are able to make the next step and consider the effects of collisional friction in differentiating between the attenuation experiences of the ordinary and extraordinary rays in their ionospheric journeys. I have always felt somewhat guilty concerning the complications which the gyroscopic terms introduce into the simple dispersion equations of Eccles and Larmor, but the experiments on the polarization of down-coming waves in England and Australia leave little doubt that we must face this difficulty.

Author's reply. The limitations arising from neglect of collisional damping in the curves given in the present paper are not apparent until the frequency of collisions is of the order of 10^5 per second, and even then the effect of friction is merely to round off the corners of the dispersion curves by removing the infinities and to prevent μ and κ from being ever actually zero. This degree of friction is most probably that pertaining to the Kennelly-Heaviside layer, at heights of 110–120 km. above the earth's surface, and the curves given in this paper may be confidently used in investigations of propagation phenomena at greater heights than this.

539.132 531.12-2

A MODEL TO ILLUSTRATE THE MOTION OF A DIATOMIC ROTATOR WITH TWO DEGREES OF FREEDOM

By LEWIS SIMONS, D.Sc. and E. H. SMART, M.A.,
Birkbeck College, London

Received November 28, 1932. *Read, with demonstration, December* 16, 1932.

ABSTRACT. An arm 5 in. long is pivoted at one end and carries at the other end a small electric lamp which is thus capable of moving on the surface of a sphere about the pivot as centre. The two angular velocities $\dot{\phi}$ and $\dot{\theta}$ can be independently controlled by two hand regulated motors: ϕ is the azimuthal and θ the co-latitudinal angular co-ordinate of the arm. If $\dot{\phi}$ and $\dot{\theta}$ are commensurable, the resulting figure traced out by the lamp remains stationary in space. This path represents the motion of one of the atoms of the rotator which has two degrees of freedom.

The apparatus is designed to show a certain class of motions of a point which possesses two degrees of freedom. The type of motion is thus defined: The point moves in a circle while the circle rotates about a fixed diameter.

The point is thus constrained to move on the surface of a fixed sphere and the
a radius a to the point has two angular velocities $\dot{\theta}$ in the circle, where θ is measured
from the fixed diameter, and $\dot{\phi}$ that of the plane of the circle about the fixed diameter.
θ We may conveniently take the fixed diameter as the polar axis: then θ is the co-
ϕ latitude and ϕ the azimuth measured from some fixed plane through the polar
axis. It is convenient at the outset to take this fixed plane such that θ and ϕ vanish
together.

n If $\dot{\theta} = n\dot{\phi}$ where n is some *commensurable* number the point P describes on the
surface of a sphere a closed path which it continually retraces. This path may be
r readily obtained if we know its projection on the equatorial plane. If r is the radius
vector of the projection of P in this plane, $r = a \sin \theta$. But, with the above-mentioned proviso, $\theta = n\phi$ if $\dot{\theta} = n\dot{\phi}$, and the equation of projection in the equatorial plane is (with ϕ as the vectorial angle) $r = a \sin n\phi$. This curve is characteristic of a class of plane polar curves known as rhodoneae from a fancied resemblance to rose petals. If n is an integer the curve consists of a number of loops passing through the origin, n in number if n is odd, $2n$ in number if n is even.

k If $\dot{\theta}$ and $\dot{\phi}$ are connected by a linear relation, say $\dot{\theta} = n\dot{\phi} + k$ where k is constant,
the effect will be to rotate the path of the point about the polar axis with an angular
t velocity $(-k/n)$, for then $\theta = n\phi + kt$ (the constant of integration may be neglected).

The figures for a number of simple cases of commensurable values of n have been drawn in figures 2 (*a*) to 2 (*f*).

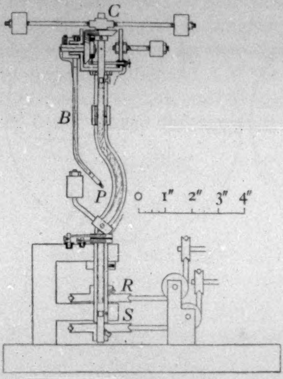


Figure 1.

The importance of this type of motion cannot be overstressed because of the attention given to it in work on molecular spectra. Here the motion occurs amongst their rotational degrees of freedom of variously constructed molecules, and, of course, the picture has been made still more complex by quantizing the motion and by expressing it in terms of wave-mechanical theory†.

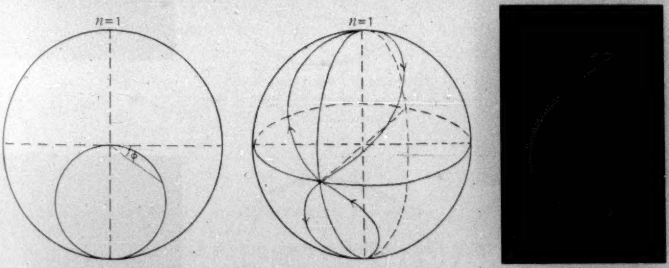


Figure 2 (*a*)*. $r = a \sin \phi$.

On account of the beauty of the motion, even with two degrees of rotational freedom, it was decided to try to construct a model to illustrate it, and figure 1

---

* The curve is the intersection of the sphere by the circular cylinder $x^2 + y^2 = ay$.

† The kinematics of a particle on the rim of a symmetrical top is a common enough subject, but the modifications introduced by quantum and wave-mechanical theory in direct application of the motion to atomic systems is dealt with by Sommerfeld, *Wave Mechanics*, p. 16 (1930); Ruark and Urey, *Atoms, Molecules and Quanta*, p. 437 (1930).

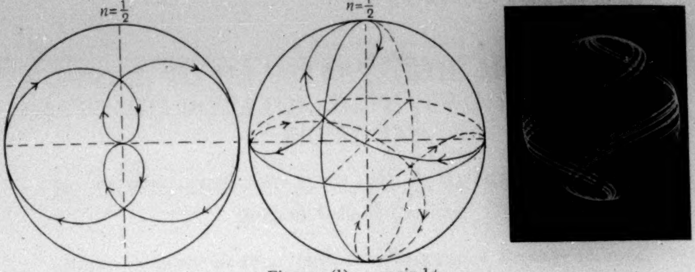

$n=\frac{1}{2}$
$n=\frac{1}{2}$

Figure 2 (*b*). $r=a \sin \frac{1}{2}\phi$.

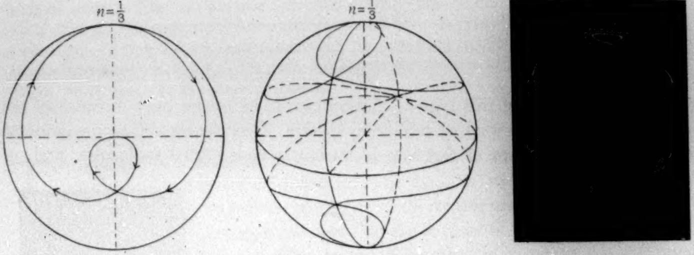

$n=\frac{1}{3}$
$n=\frac{1}{3}$

Figure 2 (*c*)*. $r=a \sin \frac{1}{3}\phi$.

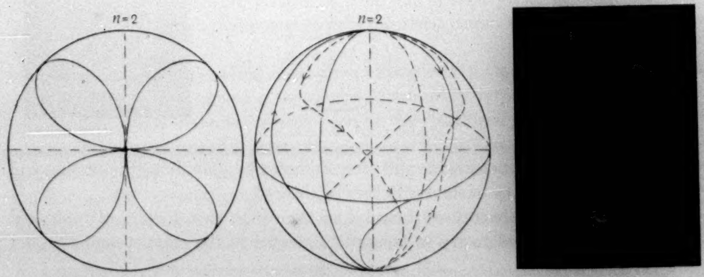


Figure 2 (*d*). $r=a \sin 2\phi$.

* Referred to its *node* as pole, this equation takes the form of the limaçon $r=\frac{1}{2}-\sin \phi$.

represents the successful attempt after some failures. It consists of a light arm *B*, 5 in. long, weighing only 1 gm., and pivoted at one end, with a small medical electric lamp *P* attached to the other end. The lamp weighs only 0·37 gm. It will be seen that *P* can move on the surface of an imaginary sphere of radius 5 in. The motions in co-latitude θ and azimuth ϕ are transmitted to the moving arm *B* by the two independently driven wheels *R* and *S*, *R* being fixed as shown to the hollow shaft and *S* to the flexible cable which runs through the hollow shaft, transmitting motion to the "fly-wheel" *C* and the connecting bevel gears. For success in working (*a*) the bend in the upright hollow shaft must enable the lamp *P* to move unhindered to any part of the spherical surface; (*b*) the vertical axis of the shaft must be a free axis so as to avoid too much vibration (loads are suitably disposed along the axis to ensure this result); (*c*) the arm *B* and its attachments must have as small a moment of inertia *I* as possible in order to minimise the gyrostatic couple $I\dot{\theta}\dot{\phi}$ that comes into play during the motion. Finally (*d*) arrangements must be made for keeping the lamp alight during the whole of its motion. The method will be obvious from the figure; the current returns from the lamp through the metal apparatus itself.

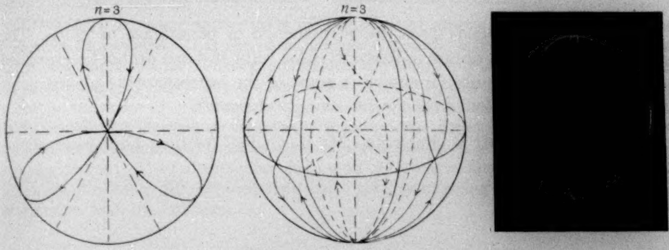


Figure 2 (*e*). $r=a\sin 3\phi$.

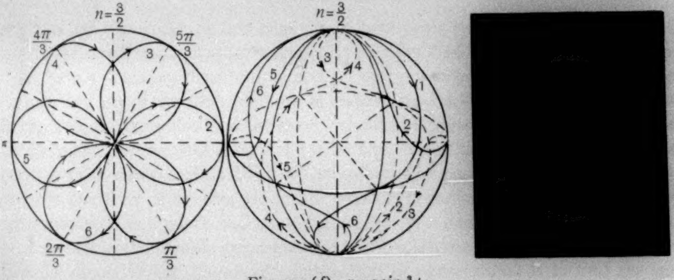


Figure 2 (*f*). $r=a\sin\frac{3}{2}\phi$.

I

Let ω_R, ω_S be the angular velocities of the wheels *R* and *S* respectively and in the same sense; then the angular velocity $\dot{\phi}$ of the lamp *P* in azimuth about the

ω_R, ω_S

vertical polar axis is ω_R, whilst the angular velocity $\dot{\theta}$ in latitude $= \omega_R - \omega_S$. The sign of ω must be changed if *R* and *S* rotate in opposite senses. If $\dot{\theta} = n\dot{\phi}$ as above, then the two possible methods of producing each figure are as shown in the table.

$n = \dot{\theta}/\dot{\phi}$	ω_R/ω_S
± 1	$0/\omega_R$ or $+2$
± 2	-1, $+3$
$\pm \frac{1}{4}$	$+\frac{3}{4}$, $+\frac{5}{4}$
$\pm \frac{3}{4}$	$+\frac{1}{4}$, $+\frac{1}{4}$

The figure seen depends upon the phenomenon of persistence of vision. The precession effect which occurs in azimuth if the ratio of $\dot{\theta}$ to $\dot{\phi}$ cannot be expressed as a commensurable number is shown in some of the accompanying photographs, which represent examples of the figures actually observed.

We wish to thank Mr F. Staley and Mr H. G. Bell for their kind assistance.

519.281.2

NOTES ON THE METHOD OF LEAST SQUARES

By Sir A. S. EDDINGTON, F.R.S.

Received November 10, 1932. *Read January* 20, 1933.

ABSTRACT. In inferring the value of a physical quantity x from observations some risk must be accepted. It is therefore presumed that the investigator has made up his mind how much risk he will take, and desires the closest possible limits—the narrowest range of values of x—that he can adopt without exceeding this risk. The aim is to furnish a concise treatment of combination of observations on this basis, which it is hoped may be found useful in clearing up common misconceptions. Stress is laid on the fact that the method of least squares is justified without the assumption of a Gaussian error law of the observations. Most of the paper deals with quite elementary points, but it ends with a discussion of more difficult questions which arise in inferring the mean square error of observation from the residuals.

§ 1. INTRODUCTION

The main purpose of this paper is to controvert two rather prevalent ideas: (1) that the method of least squares is only justified if the errors of observation have a Gaussian distribution, and (2) that the orthodox theory of errors does not sanction any of the other methods of combining observations that are often used in practice. I desire also that the theory should be presented in a way which does not introduce inverse probability. I realize that others have put forward similar or partly similar views, and probably all the substantial parts of this paper have been given at one time or another by earlier writers; nevertheless I hope that the presentation taken as a whole will show the subject in a new light to some readers*.

I think that the trouble arises because text-book writers often take it for granted that the object of the theory of combination of observations is to find *the most probable value* of the quantity x that is under discussion. This is a strange obsession, because it is difficult to imagine any circumstances in which it could be of interest to a scientist to know the most probable value of x. We must therefore insist at the outset that the purpose of the theory is to assist scientific investigation and not to answer mathematical conundrums.

What the physicist desires is *the most accurate determination* of x, in a sense which will be defined precisely in § 2. Further, although the superlative *most* may represent one aim, the more usual aim corresponds to the comparative *more*; we wish to judge of any proposed method whether it is more accurate, and how much more accurate it is, than another. No practical physicist has ever set himself to make the most accurate determination conceivable of a physical constant; he usually wishes to make a more accurate determination than his predecessors; sometimes his intention is merely to obtain a determination which is *accurate enough*, i.e. which reaches some specified degree of accuracy. The calculator may well have similar aims.

---

* The main purpose is accomplished in §§ 1–6; §§ 7–10 concern those minutiae, beloved of the mathematical theorist, which cannot be wholly omitted.

§ 2. THE "MOST ACCURATE DETERMINATION"

The meaning of "more accurate determination" is best explained by an example. Suppose that I have occasion to use Planck's constant, and I find in reference books two determinations given as

$$h \times 10^{27} = 6{\cdot}551 \pm {\cdot}013,$$
$$h \times 10^{27} = 6{\cdot}547 \pm {\cdot}008.$$

Assuming that these are to be taken at their face value, I choose the latter; but my choice is not in any way guided by the consideration that on the evidence 6·547 is more probable than 6·551. Scientific results are not used that way. If any conclusion is dependent on the choice, the first thing to bear in mind is that in all probability the true value is neither 6·547 nor 6·551. To stand a reasonable chance of being right I must employ a range of values. I therefore proceed as follows. I first make up my mind how much risk of error I am prepared to take—for with any ordinary law of errors some risk is inevitable. I decide, let us say, to take a risk of 1 in 10; this is probably not greater than the risk I habitually take in drawing inferences from observational evidence. The theory of errors tells me that for this risk I must allow $2\frac{1}{2}$ times the probable error. Accordingly I rely on the first determination as a definite assurance that the value is between 6·519 and 6·583, and the second that it is between 6·527 and 6·567. Naturally the latter is the more useful to me since it limits the value to a narrower range; it is a closer or "more accurate" determination, and will lead to sharper conclusions in the deductions that I am intending to make. Note that a "determination" is not a value, but a range of values that can be accepted with a given risk—though we often loosely apply the word to the mid-value of the range.

The accepted risk will vary according to the purpose for which the determination is to be used and the rashness of the user. A risk of $\frac{1}{6}$, corresponding to an allowance of double the probable error, is perhaps the most usual allowance for ordinary purposes; but a navigator determining his position at sea would not be satisfied to run his ship on the rocks once in six times. The practice of allowing merely the probable error as margin is not unknown—a tacit admission by the perpetrator that his habit is to tell the truth only on alternate occasions.

The "most accurate determination" should accordingly be defined by the criterion of *range per risk*. It would, however, be difficult to utilize the definition strictly in this form. It might happen that in comparing two methods of determination, one gave the more accurate determination (i.e. narrower range) when the accepted risk was small and the other the more accurate determination when the risk was large. The "most accurate determination" would then be ambiguous until the accepted risk had been specified. This is scarcely likely to occur in practice for reasons explained below; but it makes it necessary to adopt a simplified (conventional) definition for theoretical purposes, which avoids all ambiguity. We adopt the mean square error of x as the best general criterion of the accuracy of x. The criterion of mean square error will be in any case a suitable compromise between criteria based on small risks and on large risks respectively; so that it has almost the same practical utility as the criterion of range per risk that we should ideally prefer. But there is actually a better justification for using it.

When a quantity x is deduced (by any method of solution) from observational data, it has a frequency curve of error; that is to say, considering all possible ways of incidence of accidental error in the observed quantities, the resulting errors in the deduced value of x follow a frequency curve. The frequency curve of error of x must not be confused with the frequency curve of error of observation. We shall show in § 4 that in all ordinary cases the error law of x is approximately Gaussian even when the error law of observation is very far from Gaussian.

Since then in practice we have to compare determinations of x which have similar frequency curves (all being approximately Gaussian, even when the errors of observation are non-Gaussian), the possible ambiguity does not arise. The curves differ only in linear spread; and the range for given risk (whether large or small) is simply proportional to the mean square error, which can therefore be used as an equivalent measure of accuracy.

Thus the aim of the theory of combination of observations is to devise a method of solution which shall give a value of x having the smallest possible mean square error; so that we may deduce the smallest possible range of values within which x can be asserted to lie, subject to the given risk of error that we have made up our minds to accept.

§ 3. METHOD OF SOLUTION

We consider the problem of finding the most accurate determination of x from a set of equations of condition

μ, r, a, b, c, x, y, z

$$a_r x + b_r y + c_r z = \mu_r \qquad (r = 1, 2, \dots n) \qquad \dots\dots(1),$$

where μ_r has an error derived from any symmetrical* error-distribution which may differ as widely as we please from the Gaussian law. The error laws for μ_1, μ_2, etc. need not be the same, but we assume that they all have the same mean square error ϵ; if not, the equations must first be multiplied by appropriate factors so as to make the mean square error of the right-hand side the same for all, as in the ordinary process of assigning weights.

ϵ

Whatever method of finding a value of x we adopt, our value will depend on the measured quantities μ_r, so that x can be regarded as a function of the μ_r.

---

* Practical methods are generally designed to secure a symmetrical law, e.g. methods of reversal and differential measurements. But the restriction to symmetrical laws could be replaced by any other condition which excludes systematic error.

Assume for trial a linear function

$$x = \sum_r \lambda_r \mu_r \qquad \text{......(2)},$$

λ where the λ_r are arbitrary coefficients. Then, on insertion of the value of μ_r from (1)

$$x = \Sigma\lambda_r a_r . x + \Sigma\lambda_r b_r . y + \Sigma\lambda_r c_r . z \qquad \text{......(3)}.$$

This is satisfied if

$$\Sigma\lambda_r a_r = 1, \quad \Sigma\lambda_r b_r = 0, \quad \Sigma\lambda_r c_r = 0 \qquad \text{......(4)}.$$

Any set of values of λ_r which satisfies (4) will give a "solution" $x = \Sigma\lambda_r \mu_r$. It is a solution because if the measured quantities μ_r are free from error it will give the correct value of x. But when the μ_r are affected by error, these different solutions may be of widely different accuracy and we have to determine that set of values of λ_r which gives the most accurate solution.

Before proceeding further the question may be raised whether the most accurate solution is necessarily included in the linear form (2). It is quite likely that for particular non-Gaussian error laws non-linear solutions may exist which are more accurate. But it is unlikely that any non-linear method would be seriously contemplated as practicable having regard to the immense labour involved and the rarity of the occasions which call for it. An exception should, however, be noticed. When there is only one unknown and the equations of condition become simple measurements of x, "fancy methods" can be used and may be more accurate; thus, if it is known that the error law is $e^{-k|\epsilon|}d\epsilon$, the median is more accurate than the arithmetic mean, at any rate for some risks. The median is an example of a solution not included in the form (2).

If the actual error of μ_r is ϵ_r, we have by (2)

$$\text{error of } x = \Sigma\lambda_r \epsilon_r \qquad \text{......(5)},$$

and by a well-known elementary theorem (not assuming the Gaussian law)

$$\text{mean square error of } x = \sqrt{(\Sigma\lambda_r^2)} . \epsilon \qquad \text{......(6)},$$

where ϵ is the mean square error of μ_r (the same for all the μ_r's as already stated). Thus the determination of x with the smallest mean square error to be obtained by linear methods is found by making $\Sigma\lambda_r^2$ a minimum, subject to the conditions (4) being satisfied. The minimum condition, together with the conditions given by differentiating (4), gives

$$\Sigma\lambda_r \delta\lambda_r = 0 \qquad \text{......(7)}$$

for all variations $\delta\lambda_r$ which satisfy

$$\Sigma a_r \delta\lambda_r = 0, \quad \Sigma b_r \delta\lambda_r = 0, \quad \Sigma c_r \delta\lambda_r = 0 \qquad \text{......(8)}.$$

This is solved by the method of indeterminate multipliers. Suppose that

$$\lambda_r = a_r P + b_r Q + c_r R \qquad \text{......(9)},$$

P, Q, R where P, Q, R are arbitrary coefficients independent of r. Then by (9)

$$\Sigma\,(\lambda_r - a_r P - b_r Q - c_r R)\,\delta\lambda_r = 0 \qquad \text{......(10)}$$

for *all* variations $\delta\lambda_r$. But

$$\Sigma\,(a_r P + b_r Q + c_r R)\,\delta\lambda_r = 0 \qquad \text{......(11)}$$

for those variations $\delta\lambda_r$ which satisfy (8). Adding (10) and (11) we see that $\Sigma\lambda_r\delta\lambda_r = 0$ for variations $\delta\lambda_r$ which satisfy (8). Accordingly by taking λ_r of the form (9) the condition for a ***minimum*** is automatically satisfied, and it only remains to choose P, Q, R so that the conditions for a ***solution*** (4) are satisfied.

Substituting (9) in (4), we have

$$\left.\begin{aligned}\Sigma a_r^2 P + \Sigma a_r b_r Q + \Sigma a_r c_r R &= 1\\ \Sigma a_r b_r P + \Sigma b_r^2 Q + \Sigma b_r c_r R &= 0\\ \Sigma a_r c_r P + \Sigma b_r c_r Q + \Sigma c_r^2 R &= 0\end{aligned}\right\} \quad \ldots\ldots(12),$$

so that P, Q, R can be determined. Write the determinant of the coefficients of P, Q, R on the left of (12) in the standard form

$$\Delta = \begin{vmatrix} a & h & g\\ h & b & f\\ g & f & c\end{vmatrix}$$

Δ

and use capital letters for the minors of the small letters. The solution of (12) by the method of determinants is

A, *H*, *G*

$$P = A/\Delta, \quad Q = H/\Delta, \quad R = G/\Delta \quad \ldots\ldots(13).$$

Hence by (9)

$$\lambda_r = (a_r A + b_r H + c_r G)/\Delta \quad \ldots\ldots(14),$$

and by (2)

$$\begin{aligned} x &= (\Sigma a_r\mu_r . A + \Sigma b_r\mu_r . H + \Sigma c_r\mu_r . G)/\Delta\\ &= \begin{vmatrix} \Sigma a_r\mu_r & \Sigma a_r b_r & \Sigma a_r c_r\\ \Sigma b_r\mu_r & \Sigma b_r^2 & \Sigma b_r c_r\\ \Sigma c_r\mu_r & \Sigma b_r c_r & \Sigma c_r^2\end{vmatrix} \div \Delta \quad \ldots\ldots(15).\end{aligned}$$

This then is the value of x with the smallest mean square error obtainable by linear methods. It is identical with the value obtained by solving the normal equations of least squares*.

Further by (14)

$$\begin{aligned}\Sigma\lambda_r^2 &= [(\Sigma a_r^2 A + \Sigma a_r b_r H + \Sigma a_r c_r G)\,A + (\Sigma a_r b_r A + \Sigma b_r^2 H + \Sigma b_r c_r G)\,H\\ &\qquad + (\Sigma a_r c_r A + \Sigma b_r c_r H + \Sigma c_r^2 G)\,G] \div \Delta^2\\ &= [(aA + hH + gG)\,A + (hA + bH + fG)\,H + (gA + fH + cG)\,G] \div \Delta^2\\ &= (\Delta A + 0 + 0)/\Delta^2 = A/\Delta = P.\end{aligned}$$

Hence by (6)

$$\text{mean square error of } x = \epsilon\sqrt{(A/\Delta)} \quad \ldots\ldots(16).$$

This also agrees with the result of the method of least squares; in fact the coefficient A/Δ, or P, is usually found in practice by solving the equations (12).

Our results (15) and (16) thus justify the method of least squares without postulating a Gaussian error law, provided that it is understood that the method is not concerned with "most probable values." Its achievement is that (1) it gives a solution, i.e. a value which would be correct if the observations were exact; (2) it gives the mean square error of the result so that we know how wide a margin about the solution value we must allow; (3) no other linear method (and therefore no other method which we should be likely to contemplate employing) gives so small a mean square error and hence so narrow a range of x that can be trusted with an assigned risk. The conceivable existence of other methods (non-linear) giving still greater accuracy need not unduly trouble us; in practice it is more essential to know our accuracy than to crow about it.

---

* So far as the mathematics are concerned, I have utilized the method of Laplace (1811). I do not think it can be appreciated when presented apart from the argument to which I have here adapted it.

§ 4. FREQUENCY LAW OF x

By (5) the error of x is made up of n terms each involving an independent error, and in all fair applications of the method of least squares n is somewhat large. Although some of the coefficients λ may turn out to be comparatively small, a good proportion of them should be of about equal order of magnitude. For if two or three of them outweigh all the others, so that they are practically the only ones that count in the formula for x, it means that the investigator has included a mass of observational material which has practically no bearing on the determination of x, though it concerns the other unknowns in the equations of condition. He is really relying on two or three measures and not on n measures as he supposes. Thus, apart from obviously inappropriate applications of the method, we find that the error of x is the resultant of a considerable number of independent errors of more or less equal importance. It is well known that in these conditions the resultant error is approximately Gaussian even when the contributing errors (errors of observation) are non-Gaussian. The number of contributing errors need not be unduly large; 6 or 8 will give a good Gaussian curve

It is interesting to note the greater security and rigour attained when we realize that any assumption of Gaussian distribution that we require refers to the error of x and not to the errors of observation. Apart from empirical evidence, the only "proof" of the Gaussian law of errors of observation rests on the assumption that the error of observation is the resultant of many small independent errors, objective or subjective*. The assumption that the *observer*, in making his error, combines a lot of little independent errors may perhaps be defended, but it offers a favourite target to the critic; it is much more satisfactory to be able to substitute the assumption that the *calculator*, in reaching his result, combines a lot of little independent errors, for we can always examine the actual coefficients λ_r to see whether this is true, and confound (or justify) the critic.

§ 5. NON-GAUSSIAN ERRORS

It is well worth while to place our theory of combination of observations on a basis which is not restricted to observations obeying the Gaussian law, for exceptions to this law are not entirely trivial. It is well known that there is a widely prevalent cause tending to make observational errors follow the Gaussian law, viz. the combination of a large number of sources of small errors; but it is not so well known that there is a widely prevalent cause tending to bring about systematic deviation from the Gaussian law, viz. heterogeneity of observational material. This last cause operates when the data are supplied by a number of observers of different skill or by the same observer working under conditions which have varied. It gives an error law with an excess of large and small errors and a defect of intermediate errors, in comparison with the Gaussian distribution; analytically, the ratio of the fourth moment to the second moment is greater than in the Gaussian law.

---

* The proof from "the principle of the arithmetic mean," which is still sometimes quoted, is altogether fallacious.

For a Gaussian distribution the mean square error ϵ_2 and the mean fourth power error ϵ_4 are given in terms of the measure of precision h by ϵ_2 ϵ_4, h

$$\epsilon_2^2 = 1/2h^2, \quad \epsilon_4^4 = 3/4h^4 \qquad \text{......(17).}$$

Consider batches of $n_1, n_2, n_3, \ldots$ Gaussian errors with respective measures of precision $h_1, h_2, h_3, \ldots$. Then for the mixture n

$$\epsilon_2^2 = \Sigma n_r/2h_r^2 \div \Sigma n_r,$$

$$\epsilon_4^4 = \Sigma 3n_r/4h_r^4 \div \Sigma n_r.$$

Hence

$$\tfrac{4}{3}(\Sigma n_r)^2(\epsilon_4^4 - 3\epsilon_2^4) = (\Sigma n_r)(\Sigma n_r/h_r^4) - (\Sigma n_r/h_r^2)^2$$

$$= \sum_{rs} n_r n_s \left(\frac{1}{h_r^4} + \frac{1}{h_s^4} - \frac{2}{h_r^2 h_s^2}\right) = \sum_{rs} n_r n_s \left(\frac{1}{h_r^2} - \frac{1}{h_s^2}\right)^2 \qquad \text{......(18),}$$

which is a positive quantity, vanishing when the h's are all equal. Thus $\epsilon_4^4 = 3\epsilon_2^4$ for the Gaussian law, but $\epsilon_4^4 > 3\epsilon_2^4$ when batches of observations of different degrees of precision are pooled—as must usually happen in practice. It might perhaps have been thought that if the precision h were itself randomly distributed the Gaussian law would be recovered, but the formula shows that this does not happen.

§ 6. SIMPLIFIED METHODS OF SOLUTION

The investigator is free to choose for his solution any other set of values of λ_r which satisfies (4), and he often does so to save labour of calculation. His mean square error is given by (6), and his solution is a valid determination of x having the degree of accuracy thus assigned. It is necessarily less accurate than the least squares solution; but to tell him that he would have found a more accurate value by performing, say, three times as much numerical calculation is as impertinent as to tell an experimenter that he would have obtained a more accurate result by making three times as many experiments. It is not a crime to fail to reach the highest possible accuracy; it is a crime to fail to reach the accuracy which you claim.

Perhaps the commonest case in which a simple alternative to the method of least squares can safely be recommended is typified by the determination of the period T of a pendulum by observing the times t_r of n consecutive passages. The equations of condition are T, t, n

$$a + rT = t_r \qquad (r = 0, 1, 2, \ldots n-1).$$

One linear solution is obtained by comparing the mean of the first m times $(t_0, \dots t_{m-1})$ with the mean of the last m times $(t_{n-m}, \dots t_{n-1})$. The difference gives $(n-m)\,T$ with a mean square error $\epsilon\sqrt{2}/\sqrt{m}$, so that T is determined with a mean square error

$$\frac{\epsilon\sqrt{2}}{(n-m)\sqrt{m}} \qquad \text{......(19)}.$$

The weight of the determination (proportional to the inverse square of the mean square error) is therefore $\frac{1}{2}m\,(n-m)^2$. This is a maximum when $m = \frac{1}{3}n$. Hence the most accurate solution of this kind is obtained by comparing the mean of the first third against the mean of the last third of the passage times, the determination being then of weight $2n^3/27$.

The weight of the determination of the value of T by the method of least squares is, of course, rather greater; it is found to be $n\,(n-1)\,(n-2)/12$. Thus when n is large the weights of the two solutions are in the ratio 8 : 9. It is seldom that the difficulty of obtaining additional observational material is so great as to warrant the trouble of a least-squares solution for so slight a gain. The "method of thirds" is generally useful when we have to determine a slope or a linear scale-constant from more or less uniformly spread data.

§ 7. INVERSE PROBABILITY

The ordinary presentation of the method of least squares as a method of finding the most probable value of x involves an appeal to inverse probability which is difficult to justify. The argument runs as follows. If the true values of the unknowns are x', y', z', we find (from the residuals of the equations of condition) that we must have made errors $\epsilon_1', \epsilon_2', \dots \epsilon_n'$ in our observations; if on the other hand the true values are x'', y'', z'', our observational errors must have been $\epsilon_1'', \epsilon_2'', \dots \epsilon_n''$. We find further that $\epsilon_1', \epsilon_2', \dots \epsilon_n'$ is a more probable set of errors than $\epsilon_1'', \epsilon_2'', \dots \epsilon_n''$. We then introduce inverse probability, and argue that since we are more likely to have made the errors $\epsilon_1', \epsilon_2', \dots \epsilon_n'$ than the errors $\epsilon_1'', \epsilon_2'', \dots \epsilon_n''$, it is more likely that the true values are x', y', z' than that they are x'', y'', z''.

The argument that, because the consequences of hypothesis A turn out to be more probable than the consequences of hypothesis B, therefore hypothesis A is more probable than hypothesis B, cannot be accepted without qualification. Having tossed a penny 5 times in succession we observe that it has come down heads every time; this occurrence is much more probable on the hypothesis that it is a double-headed penny than on the hypothesis that it is an ordinary penny, but it does not follow that it is more probably a double-headed penny than an ordinary penny. It is true that in rejecting the argument we are guided not only by the ostensible data of the problem but by private knowledge that double-headed pennies are rare; but the real point is that questions of inverse probability are of such a nature that they compel us to introduce private knowledge or prejudice—that is to say, a priori expectation—since otherwise there is no answer to them. The objection to inverse probability is not so much that it is inadmissible as that it is silly.

The inverse-probability argument in the theory of least squares is valid only on the understanding that a priori all values of x, y, z are equally likely. Starting on this basis, we can then introduce the additional information supplied by our observations (which, of course, modifies the a priori expectation) and deduce rigorously that x', y', z' is more probable than x'', y'', z''. But we are saved any debate as to whether this hypothesis of equal a priori probability of all values of x is an admissible one, because it is easily seen that it cannot be generally true. Certain methods of determining the charge of an electron provide linear equations of condition in which the unknown quantity x is e; others yield equations of condition in which x is e^2. If all values of e are equally probable a priori, then all values of e^2 cannot be equally probable a priori; so that the hypothesis is untrue in one case. In practice the range of values of e that need seriously be considered is so small that it makes no appreciable difference whether the hypothesis of equal a priori probability refers to e or e^2 or any function of e within reason. The difficulty may not be a practical one, but it shows that the assumption underlying the use of inverse probability in the usual theory of least squares has no axiomatic basis.

This difficulty in the usual theory of least squares arises because it mixes together two distinct subjects, viz. the combination of observations and the philosophy of inference from observation. The presentation of the theory here adopted avoids the difficulty entirely because it sticks strictly to the combination of observations. It gives us a solution, say $x = x_0$, with a mean square error μ. We have first the satisfaction of knowing that it was not within our power to reduce μ by adopting any other practicable method. Secondly we may treat our result and draw just the same inferences as if we had found x_0 by a single direct observation made with mean square error μ*. Effectively then we have replaced a mass of complicated observational material by the ***best possible equivalent single direct observation*** of the quantity x that we are seeking. The task of the theory of the combination of observations ends with this reduction. Anything further that we may add belongs to the philosophy of inference from an observation. This resolves itself into a simple question—How are we justified in making any inference from an observation which is subject to error?

x_0, μ

The answer that I have adopted is as follows. We can never be sure of our inferences; therefore we have to aim at a system of inference that gives conclusons of which in the long run only $1/q$ are wrong. Accepted observational knowledge of the universe is a function of q—a series of maps becoming more and more detailed as q decreases. The maps start (at $q = \infty$) with one which is entirely trustworthy and entirely blank; and they end (at $q = 0$) with one loaded with detail of which only an infinitesimal proportion is correct. How a philosopher would use these maps I have no idea. I only affirm that some of the intermediate maps (say $q = 5$

q

---

* Except that the combination of observations has one advantage over the single observation. In drawing inferences from a single observation it is usually assumed rather hypothetically that the error law is Gaussian, but as was shown in § 4 we have much greater security that the error law of x_0 is approximately Gaussian.

to $q = 20$) can be of considerable assistance to a being who has to find his way about in the universe he lives in.

The answer given by some is that we infer (from the observation) an inverse probability of true values of x. But then, what are we to infer from the inverse probability?

§ 8. DETERMINATION OF THE MEAN SQUARE ERROR

After a least-squares solution has been made, it is usual to compute from the residuals the mean square error of an observation. I add some remarks on this part of the problem, but limit them to errors obeying the Gaussian law.

μ If μ is the mean square error computed directly from a particular sample of n errors, it can be shown that the frequency distribution of μ is

$$\mu^{n-1}\, e^{-n\mu^2/2\epsilon^2}\, d\mu \qquad \text{......(20),}$$

where ϵ is the true mean square error. The same distribution (20) is obtained when
m μ is computed from a sample of $n + m$ *residuals*, m being the number of unknowns
$\bar{\mu}$ in the equations of condition. Hence the mean value $\bar{\mu}$ of μ found from an unlimited number of such samples is given by

$$\bar{\mu} = \int_{-\infty}^{\infty} \mu^n\, e^{-n\mu^2/2\epsilon^2}\, d\mu \div \int_{-\infty}^{\infty} \mu^{n-1}\, e^{-n\mu^2/2\epsilon^2}\, d\mu$$

$$= p\epsilon \qquad \text{......(21),}$$

p where

$$p = \sqrt{\frac{2}{n}} \cdot \frac{\Gamma\left(\frac{1}{2}n + \frac{1}{2}\right)}{\Gamma\left(\frac{1}{2}n\right)} < 1 \qquad \text{......(22).}$$

The question is sometimes raised whether μ should be regarded as a determination of ϵ or of $p\epsilon$. It can be shown that its mean square deviation from ϵ is

$$\epsilon\sqrt{\{2(1 - p)\}} \qquad \text{......(23),}$$

and from $p\epsilon$ is

$$\epsilon\sqrt{(1 - p^2)} \qquad \text{......(24).}$$

Since $p < 1$, the latter is the smaller. Thus absolutely μ is a closer "shot" at $p\epsilon$ than at ϵ. But since $p\epsilon < \epsilon$, a given mean square error of $p\epsilon$ is equivalent to a larger mean square error in ϵ; and it turns out that *proportionately* μ is a closer shot at ϵ. For if we set $p\epsilon = \mu$, we determine ϵ with a mean square error

$$\frac{\epsilon\sqrt{(1 - p^2)}}{p},$$

whereas if we set ϵ equal to μ, we determine ϵ with the mean square error (23) which is easily shown to be smaller. Thus it is better to regard μ as a determination of ϵ, not $p\epsilon$.

This point is in any case rather a trivial one, and it scarcely arises when we remember that for any useful application what is needed is not a value of ϵ but a range of values which can be trusted with given risk.

§ 9. INFERENCE OF ϵ FROM μ

The problem of inference from μ is in principle the same as the problem of inference from a solution value of x already discussed. The theoretical calculation of μ reduces the mass of observational material to a single shot at ϵ. We can treat μ just as though it were a direct observation of ϵ subject to observational error. The error law is not Gaussian and is in fact slightly skew; but it is given explicitly in formula (20), so that we can find from it the range corresponding to any risk.

A practical difference, however, arises from the fact that in a determination of x the error curve of x is supposed to be independent of the value of x, whereas in a determination of ϵ the scale of the error curve of ϵ varies proportionately to ϵ. We have therefore to proceed in a rather indirect way if we are to avoid introducing inverse probability. Suppose as before that we accept a risk of $\frac{1}{10}$. From (20) we can calculate factors k, k' (functions of n) such that there is a $\frac{9}{10}$ chance that μ is between the limits ϵ/k and $k'\epsilon$. Hence having observed a particular μ, we can infer that either ϵ is between the limits μk and μ/k', or that a $\frac{1}{10}$ chance has come off. Hence if we make a practice of inferring from a determination μ that ϵ is between μk and μ/k', we shall only be wrong on those occasions on which a $\frac{1}{10}$ chance has come off—in the long run once in 10 times. Thus μk to μ/k' is the range which we can adopt with the accepted risk.

k, k'

There is a rather subtle distinction between what we have just said and the statement that the probability of ϵ being between μk and μ/k' is $\frac{9}{10}$. The latter would be a statement of inverse probability. Reverting to the example of a penny turning up heads on the first 5 throws, we can certainly infer that either the penny is double-headed or a $\frac{1}{32}$ chance has come off. But I think no one would say that the probability of its being double-headed is $\frac{31}{32}$; the probability is simply non-existent until some information as to the a priori frequency of double-headed pennies is supplied. All the same, if we pursue penny-tossing as an occupation, and habitually infer when the first 5 throws turn up heads that the penny is double-headed, and infer when a tail appears in the first 5 throws that it is not double-headed, we shall only be wrong when a $\frac{1}{32}$ chance has come off, and perhaps not then if double-headed pennies exist. Thus in the long run we shall not be wrong more than once in 32 times. The distinction is between the probability of a particular affirmation and the probability of our making a right decision by the method which led to the affirmation.

To sum up: when ϵ is known we know the frequency distribution of μ, but we cannot solve the inverse problem of finding the frequency distribution of ϵ when μ is known. The latter is not required because we can infer directly from μ a range of ϵ, subject to the inevitable limitation that a specified proportion of our inferences by this method will be wrong.

§ 10. COMBINED INVESTIGATION OF x AND ϵ

In writing down the range of x which can be accepted with given risk, we use the mean square error of x, viz. $\epsilon\sqrt{(A/\Delta)}$, which is known in terms of the mean square error of an observation ϵ. But if ϵ itself is inaccurately known and can be specified only as a range (subject to risk), a complicated problem arises as to how to combine risks in ϵ and risks in x. Owing to the fact that a rather large number of residuals are needed in order to determine ϵ at all sharply, this is not always a pedantic objection. There is therefore considerable interest in the theory (now often preferred) by which the frequency distribution of x is found directly in terms of the observed mean square error μ instead of in terms of the true mean square error ϵ whose value is uncertain. I think, however, that this theory has not been extended to non-Gaussian errors of observation.

This undoubtedly is the more logical procedure when x and ϵ are determined *from the same data*, as is often the case. But it would not be quite fair to the ordinary theory of least squares to regard it as superseded by this modern refinement. More especially in those problems of astronomy and geodesy which form the traditional field of application of the theory of errors, the determination of ϵ rests on much more extensive data than the determination of x; so that the determination of ϵ and the determination of x are separate problems as here assumed. From the practical point of view, adequacy of data is more important than mathematical polish. For example, astronomers determining a hundred or more stellar parallaxes used to calculate the probable error of each parallax from its own residuals; it has been realized that this is very wasteful of accuracy, and nowadays the probable errors of the separate parallaxes are based on a common value of ϵ obtained from the residuals of the whole series. Thus the determination of ϵ employs more than a hundred times as many data as the determination of an x.

I have therefore felt justified in ruling the rigorous combined treatment of ϵ and x to be outside the scope of this paper, regarding it as an incidental rather than a basic problem in the theory of least squares.

DISCUSSION

Dr N. R. Campbell. I agree so entirely with the author's conclusions that I hesitate to criticize his arguments. But the following considerations seem to support rather than to contradict them.

(1) The author says rightly that the physical problem is always to select a range of values. He implies, rightly again, that, in using the selected range to test the truth of a physical proposition, it is always assumed tacitly that all values within this range are equally probable. If so, the application to physical problems of a theory whose aim is "to devise a method...which shall give *a* value of x..." (uniquely distinguished) must involve logical inconsistency. Such a theory cannot, therefore, be used to *prove* anything physically important; it can only *suggest* something to be established by other means.

(2) The assumption that probability is determined by the mean square error is convenient and often legitimate. But there is no evidence that it is accurately true. Consequently it may be expected sometimes to exclude permissible methods and sometimes to justify impermissible methods. Thus the "method of thirds" must be wrong; for the best method of using a group of equally trustworthy observations can never be to ignore completely one-third of them. This is important, because the theory of errors is the last surviving stronghold of those who would reject plain fact and common sense in favour of remote deductions from unverifiable guesses, having no merit other than mathematical tractability.

(3) Six or eight observations will *not* give a good Gaussian curve; six or eight millions will not do so. For the Gaussian curve is continuous, while the frequency curve of observations must be discontinuous, because the number of alternative readings on any instrument whatever must be finite. Again, the assumption of continuity is sometimes permissible; but, once more, experience shows that it is likely to be used most confidently when the evidence against it is most overwhelming. (See R. T. Birge's recent papers.)

Inst.-Capt. T. Y. Baker. May I plead for a more explicit statement on the part of authors of scientific papers as to what they mean when they sum up the result of a series of measurements as $a \pm b$? For I am sure that the conventions that underlie, or ought to underlie, this summarization are often unknown to the reader and sometimes to the author. I believe that a is, conventionally, the algebraic mean of the n values and b is $\mu/\sqrt{n}$, where μ is the mean square error. That is to say, if r is a typical residual, $\mu = \sqrt{(\Sigma r^2/n)}$, so that $b = \sqrt{(\Sigma r^2)}/n$. I am pretty certain that b does *not* always have this value and may on occasion stand for probable error, or mean error, or mean square error, or even for some multiple of one of these. Doubtless to anyone continually engaged on work of a statistical nature, and who is frequently applying the methods of the theory of errors, no ambiguity is likely to arise, but so many people who read the journals of scientific societies have no intimate knowledge of that branch of mathematics. The risk of the expression $a \pm b$ being misunderstood is so great that I feel sure an author would be doing a great kindness to his readers if he would always state, quite clearly, exactly what he means when he puts down an expression of this character. Let me give an example of the way in which a misunderstanding may arise. In a dimensioned engineering drawing $a \pm b$ is very frequently used. The nominal dimension is a; b is the tolerance either way. An engineer looking up the value of Planck's constant, mentioned in § 2, might, quite naturally, infer that $h \times 10^{27}$ might lie anywhere between 6·538 and 6·564, according to one authority, and between 6·539 and 6·555 according to another, whereas the limits that connote practical certainty are wider.

One cannot have the whole of a series of measurements printed *in extenso*, and if a convention as to the meaning of b is required I suggest that the mean error of a single observation has much to recommend it. In the first place, the mean error involves less labour in its computation and furnishes a check, in the equality of the sums of the positive and negative residuals, on the accuracy of the arithmetic. With the very limited number of observations to which the Gaussian law of errors is so often applied, the modulus of the curve may, for all practical purposes, be derived just as well from the mean error as from the mean square error. In the second place, the mean error gives simple factors for the ranges corresponding to risks of 1 in 10, 1 in 100 and 1 in 1000. They are respectively 2, 3 and 4 times the mean error. Thus, expressed in this manner, $a \pm b$ indicates immediately that there is one chance in 10 that the value of a single observation lies outside the range $a - 2b$ to $a + 2b$, one chance in 100 that it lies outside the range $a - 3b$ to $a + 3b$, and one chance in 1000 that it lies outside the range $a - 4b$ to $a + 4b$. These numbers are only approximate; more accurately they should be 2·06, 3·22 and 4·14, but the round figures are generally good enough for practical purposes.

Finally I would urge physicists not only to explain at the head of every paper what they mean by $a \pm b$, but also to make a point of giving the number of observations in each case.

Mr J. Guild. This paper is one which will be read with great interest by experimental physicists: it would undoubtedly have given rise to a prolonged and useful discussion had it been presented otherwise than as one item in a rather congested programme.

It is gratifying to find such an eminent mathematician as the author agreeing that there is no validity in the Gaussian law as applied to errors of observation. Practical physicists have challenged it before, on the ground that it bears no relation whatever to the circumstances in which errors of observation arise, but little attention appears to have been paid to them. N. R. Campbell* rejects the Gaussian theory of error "without qualification and with the utmost possible emphasis; and with it...all theoretical grounds for adopting the rules that are based on it." His reasons for doing so must appeal to all practising physicists as in complete accordance with the facts of their own experience if they have troubled to give any thought to the matter at all. Any theory based on an assumed law for the distribution of observational errors must be ruled out of court.

I am glad to note, also, that the author effectively disposes of the meaningless old bogey, "most probable value," but would have liked him to make a similar clearance of the term "probable error," which is a source of great confusion and seems to me to have no more justification than the other.

Having discarded the Gaussian law as applied to observational errors, the author reintroduces it as applied to the error of x, where x is the value of the thing measured, deduced from a series of observations each subject to a small independent error, and he re-establishes the method of least squares on this basis. It would appear that under circumstances, if such ever exist, in which we can agree in advance that the observational errors are "independent" no exception can be taken to this process. I would not like to say that such circumstances never exist, but I would hesitate equally to admit that I had ever met them. On the other hand, one can assert with certainty that in at least many, if not all, of the cases which arise in laboratory physics there is no such thing as an entirely independent error. Errors of the type we are here considering, namely those which produce a spread in the observations, arise from failure in one or all (usually all) parts, human and mechanical, of the experimental system to behave in an absolutely identical manner under immediately identical circumstances. Past history affects the behaviour not only of the human observer but of every constituent part of the apparatus. I suppose, however, that independence of the errors, as such, does not enter into the author's argument, provided that, whether independent or not, they give rise to an approximately Gaussian distribution in the resulting values of x; and the advantage of this criterion, as the author points out, is that the computer can always see whether it is satisfied or not in any particular case.

---

* *Measurement and Calculations*, p. 162.

I am not convinced, however, that even then Campbell's case against the Gaussian method of reduction has been invalidated. It is generally admitted, except possibly by rabid statisticians, that no method of reduction of experimental observations can give an answer which has any significance within limits which are *very* much closer than the uncertainty of the individual observations. This is certainly the case in all laboratory work, where time and other considerations prevent the enormous series of observations, with which the statistician loves to work, from being made; and no competent experimenter would ever attach significance to the *difference* between the results deduced from a given series of observations by different legitimate methods; he would always use the method which involves the least arithmetic, such as taking the mean value of the relevant variable. If the difference between this and any other feasible result based on the observations is comparable with the range per risk at which he is aiming, his time will be much better spent in improving his technique, so as to get better observations, than in making lengthy calculations.

With regard to the evaluation of range per risk as a criterion of the reliability of a determination, I submit that "probable error," or any other function of the non-systematic errors, is entirely valueless. The risk of the true result being outside any given limits is surely as much dependent on systematic error as on the spread of the observations. No theory of errors which aims at obtaining formulae can take systematic error into account. The mathematician generally assumes that it is the business of the experimenter to eliminate all systematic errors. So it is, and he does so as completely as he can; but when the precautions suggested by his experience and permitted by his available equipment are exhausted some sources of systematic error still remain and, from the point of view of the experimenter who is doing his best to measure something, such unsuspected errors are as much accidental as those which merely affect the precision of repetition. They are a much more serious problem to him, or to anyone else who wants to estimate the accuracy of the result. Criteria of precision may have been of great importance in the early days of experimental science when relatively crude and insensitive instruments had to be used, but nowadays it is nearly always possible in any type of measurement to get more precision than has any significance in the final result. The elusive fiend—systematic error—is the crucial thing in modern laboratory work, and the man who estimates the value of his own determinations by any function of the precision is merely singing himself to sleep with a pretty formula. As the result of twenty years' experience in a laboratory where accuracy is the primary object in all the work carried out, I would attach absolutely no importance whatever to ± limits, based on root-mean-square error or any other function of non-systematic error, placed after results obtained either by myself or anyone else. If I were faced with the particular problem put by the author at the beginning of paragraph 2, I would take no notice of the ± 0·008 or ± 0·013. I would first read carefully through the papers of both men and form some idea for myself of the relative merits of their technique and of their experience in work of this kind. If they happened to be well-known men I would supplement my own judgment by consideration of the instances known to me in which their work had been contradicted or corroborated by others of similar status, and from these various considerations I would acquire a greater amount of faith in one result than in the other. I might, of course, be wrong in any particular case, but in the long run I should be more often right than wrong because I am taking into account the really relevant factors, and this is what no formula based on mere precision of observations can ever do.

Mr T. SMITH. Sir Arthur Eddington is very closely associated with a science in which very effective use has been made of the theory of errors. His views will interest even those who consider this theory of no importance so far as their own branch of work is concerned, and in this number are several members of the N.P.L. staff. Assuming, however, that there are types of measurement carried out at the N.P.L., or similar standardizing institutions, where the theory can properly be applied, what does Sir Arthur consider a reasonable risk for them to run in giving results? Since these results are given for use outside the Laboratory, the risk is not a matter which concerns the staff alone.

I should also like to ask Sir Arthur to give his views on the application of the theory to the following problem. Two potential differences, each in the neighbourhood of 100 volts, are to be compared, and the comparison is to be correct (the risk, say, being that permissible for a standardizing laboratory to run) to 0·1 volt, so that the tolerance is represented by ± 0·05 volt. The only instrument available at the moment for the comparison is a correctly graduated voltmeter, which, however, has the property that the pointer will not move from a given position unless the voltage changes by at least 1 volt, and that the pointer, owing to grit, to inertia, or other causes, may come to rest at any place within $\frac{1}{2}$ volt of the applied potential difference. Stated in this form the problem may seem frivolous, but it represents a class of real problems on which divergent views are held, and some of us would like to hear the author's.

AUTHOR's reply. I am very pleased that the paper should have drawn so interesting a discussion. In reply to Dr Campbell's points as numbered: (1) I said, the aim of the theory is "to devise a method...which shall give a value of x...so that we may deduce a range...." By omitting the last words Dr Campbell makes it appear that the final result is *a* value instead of a range, contrary to the whole tenor of the paper. I do not anywhere assume or imply that values within the range are equally probable; in general, that is far from true. Anything less than the whole range corresponds to a risk greater than we can accept, so that no question of subdividing the range arises. (2) As Mr Guild points out, there is no object in reducing the accidental error much below the unavoidable systematic errors; so when the method of thirds reaches this limit of accuracy there can be no justification for preferring more complicated methods. In any case I object to describing a method as "wrong" merely because a more accurate result could have been obtained by additional labour. By that standard all quantitative experimental results are wrong. (3) I did not say that 6 or 8 observations give a good Gaussian curve. I said that 6 or 8 contributing errors (combined in each observation) give a good Gaussian curve.

Inst.-Capt. T. Y. Baker comments on the ambiguity of $\pm b$, when no indication is given as to whether b is mean square error, probable error, etc. One's knowledge of human nature is usually a sufficient guide—bearing in mind that the probable error is the smallest of the lot.

In reply to Mr Guild: The argument (both in the deduction of the Gaussian law for x, and elsewhere) assumes the errors to be independent. When errors occur in runs of one sign, as they sometimes do, I am afraid the calculator cannot do much—except blame the experimenter. In his criticism of the theory of errors, Mr Guild seems to have in mind mainly quantities obtained by direct measurement, where (after reading an account of the methods and precautions) one can judge from experience the sort of accuracy likely to be attained. But this is not typical of the method of least squares. I do not think anyone could form an idea of the accuracy of a quantity like h, which is indirectly determined, without going through the calculations. When a probable error has been calculated, we may employ our judgment of men and methods as to whether it should be accepted at its face value; but our judgment must be given something to work on.

In reply to Mr T. Smith: The admissible risk varies enormously with the instrument. In testing clinical thermometers you must consider what proportion of users you are prepared to kill by misleading the doctor. In testing taximeters you may justifiably take a somewhat higher risk of permitting overcharge. I am afraid the second question is too technical for me.

621.314.234:621.43.047

THE CONTROL OF IGNITION-COIL DISCHARGE CHARACTERISTICS

By G. I. FINCH and R. W. SUTTON
Imperial College of Science and Technology

Received November 2, 1932. *Read, with demonstration, January* 20, 1933.

ABSTRACT. The theory of the ignition coil is developed and is verified by means of the cathode-ray oscillograph. It is known that the secondary discharge consists of two parts, the "capacity" component due to the discharge, upon breakdown of the spark gap, of the energy stored in the secondary capacity, and the subsequent discharge of the electromagnetically stored energy, the so-called "inductance" component. It is shown that the spark-gap voltage is constant throughout the life of the inductance component, and that the inductance-component current is oscillatory but unidirectional.

The theory leads to the conclusion, confirmed experimentally, that the closing of the primary circuit during the life of the inductance component rapidly extinguishes the secondary discharge. A contact-breaker enabling the duration of opening of the primary circuit to be controlled with accuracy over a range between 0 and 4 msec. is described. The elimination of various portions of an ignition-coil discharge without material effect upon the remainder of the discharge is discussed.

---

§ 1. INTRODUCTION

It is well known that the ignition-coil discharge is a complex phenomenon, consisting in general of at least two parts, namely the so-called "capacity" component due to the discharge of the secondary self-capacity on the breakdown of the gap, and the subsequent discharge of electromagnetic energy stored in the secondary and known generally as the "inductance" component of the coil discharge. It is clear, therefore, that a systematic study of coil ignition would require that the rôles played by the capacity and inductive components be investigated individually. In order to do this, it would be necessary to be able to arrange conditions in such a manner that the discharge component not under examination could be completely suppressed and the other modified as required and in a known manner.

In what follows, an account is given, inter alia, of a method developed from the analysis of the ignition-coil circuit, by means of which the inductive component of the coil discharge can be either wholly or in part suppressed without modifying the preceding part of the discharge.

§ 2. THE THEORY OF THE IGNITION COIL WITH SPECIAL REFERENCE TO THE INDUCTIVE COMPONENT OF THE DISCHARGE

For analytical purposes, the circuit to be considered is that shown in figure 1. The conditions to be investigated are those which obtain immediately after the opening of the break.

The secondary-circuit resistance being neglected, the general circuit equations are as follows:—

$$L_1 di_1/dt + L_{12} di_2/dt + R_1 i_1 + e_1 = 0 \qquad \text{......}(1\,a),$$

and

$$L_2 di_2/dt + L_{21} di_2/dt + e_2 = 0 \qquad \text{......}(1\,b),$$

where L_1, L_2 and C_1, C_2 are the primary and secondary inductances and capacities respectively, R_1 is the primary resistance, i_1 and i_2 are the primary and secondary currents, e_1 and e_2 are the potential differences between the plates of the condensers C_1 and C_2, L_{12} and L_{21} are the coefficients of induction of the secondary on the primary and of the primary on the secondary respectively, and t is the time.

L_1, L_2, C_1, C_2
R_1, i_1, i_2
e_1, e_2
L_{12}, L_{21}

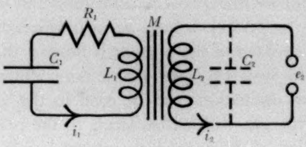


Figure 1.

The complete analysis of these equations has been carried out by Taylor-Jones* for two cases, namely (i) open-circuit secondary with no discharge passing and (ii) secondary shunted by an ohmic resistance, with the main object of determining the adjustments necessary in order to obtain the greatest possible secondary potential. The requirements governing the design of an ignition coil are, however, of a different nature, because such a coil is required to furnish a spark across a fixed gap the breakdown potential of which is considerably smaller than the maximum potential which the coil can deliver. Hence the solutions to the above general circuit equations, as given by Taylor-Jones, cannot be directly applied to the case of an ignition coil, where the secondary is shunted by a spark. A solution for this case could, however, be obtained, provided the (voltage, current) characteristic of the discharge were known.

The relationship between voltage and current in an induction-coil spark discharge does not appear to have been determined hitherto, although it is well known that the discharge cannot be even approximately represented by an ohmic resistance. Accordingly it was decided to determine the (voltage, current) characteristic of the discharge directly by means of a cathode-ray oscillograph.

Numerous oscillograms were taken of the secondary current and of the voltage across the electrodes of a gap traversed by the ignition-coil discharge, a wide range of gap-widths and primary currents being employed for this purpose. In obtaining the oscillograms of the secondary current, the oscillograph plates were connected across a 3040-Ω. non-inductively wound wire resistance in series with the spark gap and secondary. A suitably tapped 4-MΩ. Siemens Draht resistance across the spark gap served as potential-divider in securing the voltage oscillograms. Spherical (diameter 0·75 cm. brass), crossed-wire (no. 18-s.w.g. nickel or copper), and needle-point-sphere (needle-point the cathode and sphere the anode) spark gaps were employed.

---

* *The Theory of the Induction Coil* (London, Pitman and Sons, 1932).

A result typical of the range of conditions thus examined is reproduced in the oscillogram recorded in figure 4. This shows that the inductive component of the secondary current executes damped oscillations of considerable amplitude, but is throughout unidirectional. The voltage across the gap (figure 2 *a*) rises rapidly to a high value, the breakdown potential of the gap, and then falls with such extreme rapidity as to leave no trace on the oscillogram to a much lower value e_2, at which it remains practically constant throughout the remainder of the discharge. The oscillations occurring at the end of the voltage trace are not set up until the secondary current ceases to flow and are merely oscillations forced in the secondary. Thus the virtual constancy of the secondary voltage persists throughout the period during which the inductive component of the current is flowing through the gap, in spite of the fact that the current is varying over a wide range during this period. No sign of the secondary-current oscillations can be seen in the voltage trace, except in the extreme case when the gap-width is so large, or the primary current so small, that each single oscillation of the secondary current is followed by the extinction of the discharge. In this case, as is clearly seen in figure 2 *b*, the voltage rises afresh to the breakdown value of the gap at the beginning of each oscillation of the inductive component current, whereupon it immediately falls to the low constant value and remains there during the rest of the current oscillation.

The above oscillograms show clearly that as long as current is flowing the voltage across the gap is constant to within the practical limits of accuracy of the cathode-ray oscillograph employed.

On breaking the primary circuit, the primary current, which has an initial value
i_0 of i_0, commences to fall, and the induced secondary current charges up the secondary capacity to the breakdown voltage of the gap. The secondary capacity thereupon discharges through the gap, forming the capacity component of the discharge. Its duration is so brief that, as is shown in figures 2 *a* and 2 *b*, the cathode-ray oscillograph fails to record a visible trace of its passage, although the fact that the inductive component current trace in figures 4, 6 *a* and 6 *b* never begins at, but always some distance above, the origin affords sufficient testimony to its existence. We are, therefore, justified in assuming that, for all practical purposes, from the moment of breakdown of the gap (when the primary
i_p current has a value i_p, which is less than the initial value i_0 by an amount depending upon the energy absorbed in charging up C_2 to the breakdown potential of the gap) the secondary voltage has a value e_2 which remains constant so long as the secondary current is flowing through the discharge and has a finite positive value.

PHYSICAL SOCIETY, VOL. 45, PT. 2 (FINCH AND SUTTON)

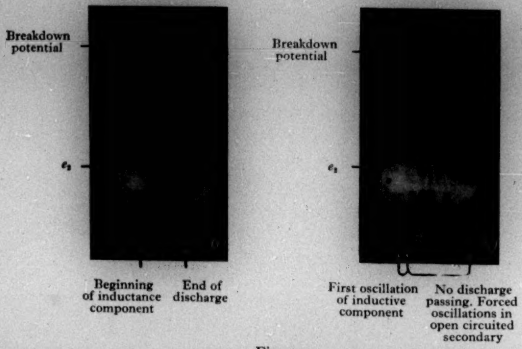


Figure 2.

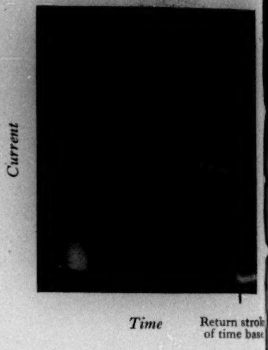


Figure 3.

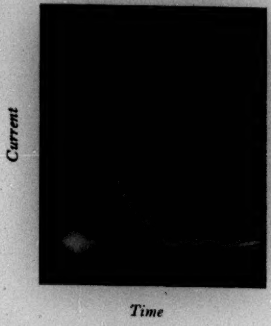


Figure 4.

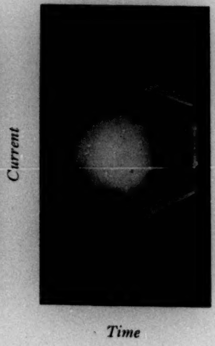


Figure 5.

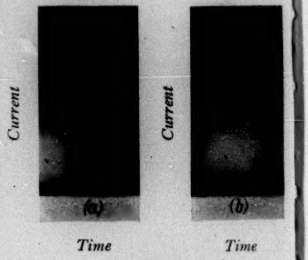


Figure 6.

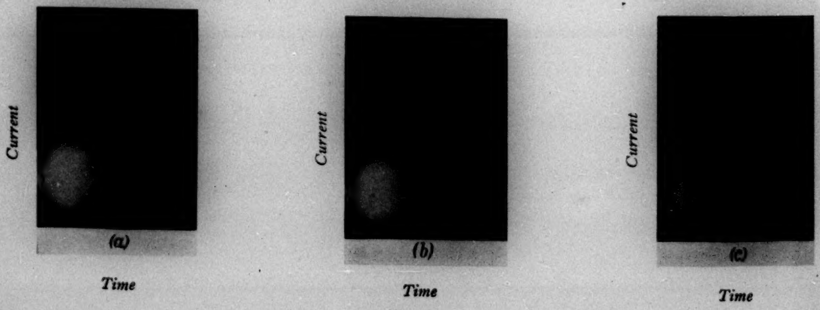


Figure 7.

Therefore no current flows in the secondary self-capacity throughout this period. It follows that the current-distribution in the secondary winding is uniform, and hence $L_{12} = L_{21} = M$. The general circuit equations can now be readily solved as follows:— M

$$L_1 d^2q_1/dt^2 + Md^2q_2/dt^2 + R_1 dq_1/dt + q_1/C_1 = 0,$$

and

$$L_2 d^2q_2/dt^2 + Md^2q_1/dt^2 + e_2 = 0,$$

where $q_1 = \int i_1 dt$ and $q_2 = \int i_2 dt$. q_1, q_2

These equations may be written in the form

$$(L_1D^2 + R_1D + 1/C_1)\,q_1 + MD^2q_2 = 0 \qquad \text{......}(2a),$$

and

$$MD^2q_1 + L_2D^2q_2 = -e_2 \qquad \text{......}(2b),$$

where D is the operator d/dt. D

Eliminating q_1, and putting $M^2 = \kappa^2 L_1 L_2$, we obtain κ

$$\{D^2(D^2 + aD + b)/(1 + R_1C_1D + L_1C_1D^2)\}\,q_2 = -e_2/L_1L_2C_1(1-\kappa^2),$$

where

$$a = R_1/L_1(1-\kappa^2),$$

a

and

$$b = 1/L_1C_1(1-\kappa^2).$$

b

The complete solution for q_2 is, therefore,

$$q_2 = A_2 + B_2t - e_2t^2/2L_2 + P_2e^{m_1t} + Q_2e^{m_2t},$$

where

$$m_1 = -a/2 + (a^2/4 - b)^{\frac{1}{2}},$$

m_1

$$m_2 = -a/2 - (a^2/4 - b)^{\frac{1}{2}},$$

m_2

and A_2, B_2, P_2, Q_2 are arbitrary constants. A_2, B_2, P_2, Q_2

Similarly, eliminating q_2 from equations $(2a)$ and $(2b)$ and substituting $M^2 = \kappa^2 L_1 L_2$, we obtain

$$(D^2 + aD + b)\,q_1 = Me_2/L_1L_2(1-\kappa^2).$$

The complete solution for q_1 is, therefore,

$$q_1 = MC_1e_2/L_2 + P_1e^{m_1t} + Q_1e^{m_2t},$$

where P_1 and Q_1 are arbitrary constants. P_1, Q_1

The solutions of the original differential equations are thus

$$q_1 = MC_1e_2/L_2 + P_1e^{m_1t} + Q_1e^{m_2t} \qquad \text{......}(3a),$$

and

$$q_2 = A_2 + B_2t - e_2t^2/2L_2 + P_2e^{m_1t} + Q_2e^{m_2t} \qquad \text{......}(3b).$$

Differentiating these equations, we get

$$i_1 = m_1P_1e^{m_1t} + m_2Q_2e^{m_2t} \qquad \text{......}(4a),$$

and

$$i_2 = B_2 - e_2t/L_2 + m_1P_2e^{m_1t} + m_2Q_2e^{m_2t} \qquad \text{......}(4b).$$

By substituting the expressions obtained for q_1 and q_2 in the two original differential equations, the following two relations between the six arbitrary constants are obtained:—

$$MP_1 + L_2P_2 = 0 \qquad \text{......}(5a),$$

and

$$MQ_1 + L_2Q_2 = 0 \qquad \text{......}(5b).$$

The remaining four relations follow from the initial conditions which are that, when the time $t = 0$,

q_p

$$q_1 = q_p = C_1 e_p,$$

$$q_2 = 0,$$

$$i_1 = i_p,$$

and

$$i_2 = i_s,$$

e_p i_p, i_s where e_p is the potential difference between the plates of the primary condenser, and i_p and i_s are the primary and secondary currents, at the moment of breakdown.

The relations given by the initial conditions are

$$P_1 + Q_1 + MC_1 e_2/L_2 = C_1 e_p \qquad \ldots\ldots(5c),$$

$$A_2 + P_2 + Q_2 = 0 \qquad \ldots\ldots(5d),$$

$$m_1 P_1 + m_2 Q_1 = i_p \qquad \ldots\ldots(5e),$$

and

$$B_2 + m_1 P_2 + m_2 Q_2 = i_s \qquad \ldots\ldots(5f).$$

The six equations, (5*a*) to (5*f*), determine the arbitrary constants, as follows:—

$$A_2 = nC_1 (e_p - ne_2),$$

$$B_2 = i_s + ni_p,$$

$$P_1 = \{i_p + m_2 C_1 (ne_2 - e_p)\}/(m_1 - m_2),$$

$$Q_1 = \{i_p + m_1 C_1 (ne_2 - e_p)\}/(m_2 - m_1),$$

$$P_2 = -nP_1,$$

$$Q_2 = -nQ_1,$$

n where $n = M/L_2$.

In all practical cases, $b > a^2/4$, and $(a^2/4 - b)^{\frac{1}{2}}$ is, therefore, imaginary. On substituting the above values for the arbitrary constants and converting exponentials to circular functions, equations (4*a*) and (4*b*) become

$$i_1 = e^{-at/2} \{i_p \cos \omega t + I \sin \omega t\} \qquad \ldots\ldots(6a),$$

and

$$i_2 = i_s + ni_p - e_2 t/L_2 - ne^{-at/2} \{i_p \cos \omega t + I \sin \omega t\} \qquad \ldots\ldots(6b),$$

ω where

$$\omega = (b - a^2/4)^{\frac{1}{2}},$$

I and

$$I = \{2 (ne_2 - e_p)/R_1 - i_p\}\, a/2\omega.$$

The voltage across the primary condenser is given by $e_1 = q_1/C_1$, i.e.

$$e_1 = ne_2 - e^{-at/2} \{(ne_2 - e_p) \cos \omega t - E \sin \omega t\} \qquad \ldots\ldots(6c),$$

E where

$$E = i_p/\omega C_1 - (ne_2 - e_p)\, a/2\omega.$$

These solutions can be written in the forms

$$i_1 = (i_p{}^2 + I^2)^{\frac{1}{2}} e^{-at/2} \cos (\omega t - \phi) \qquad \ldots\ldots(7a),$$

$$i_2 = i_s + ni_p - e_2 t/L_2 - n (i_p{}^2 + I^2)^{\frac{1}{2}} e^{-at/2} \cos (\omega t - \phi) \qquad \ldots\ldots(7b),$$

and

$$e_1 = ne_2 - \{(ne_2 - e_p)^2 + E^2\}^{\frac{1}{2}} e^{-at/2} \cos (\omega t + \theta) \qquad \ldots\ldots(7c),$$

ϕ where

$$\tan \phi = I/i_p,$$

θ and

$$\tan \theta = E/(ne_2 - e_p).$$

The resistance of the secondary circuit has been neglected in deriving these equations which represent the inductive component of the discharge in terms of the coil constants, of the instantaneous values of primary and secondary current, and of primary voltage, at the moment of breakdown of the gap. The great simplification attained thereby is fully justified by the fact that the experimental results set forth below show, as was indeed to be expected, that the voltage-drop across the secondary-circuit resistance is always small in comparison with e_2.

Although exact numerical solutions of these equations cannot be obtained without a knowledge of the instantaneous values of the primary and secondary currents at the moment of breakdown of the spark gap, there are two particular cases for which they can be simplified. They are:—

Case 1. *Secondary short-circuited.* In this case $e_2 = 0$, $e_p = e_0$, and $i_p = i_0$, where e_0 and i_0 are the primary voltage and current respectively, at the moment of breaking the primary circuit. The equations now reduce to

e_0, i_0

$$i_1 = (i_0^2 + I^2)^{\frac{1}{2}} e^{-at/2} \cos(\omega t - \phi),$$

$$i_2 = i_s + ni_0 - n(i_0^2 + I^2)^{\frac{1}{2}} e^{-at/2} \cos(\omega t - \phi),$$

and

$$e_1 = -(e_0^2 + E^2)^{\frac{1}{2}} e^{-at/2} \cos(\omega t + \phi).$$

Now,

$$\begin{aligned} I &= -(i_0 + 2e_0/R_1)\, a/2\omega \\ &= -i_0(1 + 2e_0/R_1 i_0)/\{4L_1(1-\kappa^2)/R_1^2 C_1 - 1\}^{\frac{1}{2}}, \end{aligned}$$

and

$$\begin{aligned} E &= i_0/\omega C_1 + ae_0/2\omega \\ &= i_0/\omega C_1 + e_0/\{4L_1(1-\kappa^2)/R_1^2 C_1 - 1\}^{\frac{1}{2}}. \end{aligned}$$

Since, in practice, $R_1^2 C_1/4L_1(1-\kappa^2)$ is less than $0{\cdot}001$, we may neglect I in comparison with i_0 and may write $E = i_0/\omega C_1$.

Moreover, since $e_0 \doteqdot i_0 R_1$,

$$\begin{aligned} e_0/E &\doteqdot \omega R_1 C_1 \\ &\doteqdot [\{R_1^2 C_1/L_1(1-\kappa^2)\}\{1 - R_1^2 C_1/L_1(1-\kappa^2)\}]^{\frac{1}{2}} \\ &\doteqdot 0. \end{aligned}$$

Therefore e_0 may be neglected in comparison with E.

With the above approximations, the equations reduce to

$$i_1 = i_0 e^{-at/2} \cos \omega t \qquad \text{......(8}a\text{)},$$

$$i_2 = ni_0\{1 - e^{-at/2} \cos \omega t\} \qquad \text{......(8}b\text{)},$$

and

$$e_1 = (i_0/\omega C_1)\, e^{-at/2} \sin \omega t \qquad \text{......(8}c\text{)}.$$

It is thus apparent that in this case the primary current executes a series of damped oscillations about zero, having an initial amplitude equal to the current at break. The primary voltage executes damped oscillations of initial amplitude $i_0/\omega C_1$ about zero. The secondary current rises to a maximum value $2i_0 e^{-a\pi/2\omega}$ and executes damped oscillations of initial amplitude ni_0 about a mean value ni_0. In practice, an exponential decay curve must be superimposed on these oscillations, owing to the presence of resistance in the secondary circuit.

Case 2. *Coil under working conditions.* In this case the primary current is considerably in excess of the minimum value required to produce a secondary e.m.f. sufficient to break down the gap. The energy absorbed from the primary in charging up the secondary capacity to the breakdown potential of the gap is only a small fraction of the total primary energy. We may therefore assume that $i_s = 0$, $i_p = i_0$, and $e_p = e_0$. Since ne_2 is in general of the same order as e_0, we may, as in case 1, neglect I in comparison with i_0 and $(ne_2 - e_0)$ in comparison with E. The equations therefore become

$$i_1 = i_0 e^{-at/2} \cos \omega t \qquad \text{......(9}a\text{)},$$

$$i_2 = ni_0 \{1 - e^{-at/2} \cos \omega t\} - e_2 t/L_2 \qquad \text{......(9}b\text{)},$$

and

$$e_1 = ne_2 + (i_0/\omega C_1)\, e^{-at/2} \sin \omega t \qquad \text{......(9}c\text{)}.$$

The axis of the secondary-current oscillations is given by

$$i_2 = ni_0 - e_2 t/L_2 \qquad \text{......(10)},$$

and the total duration τ of the secondary current by

$$\tau = Mi_0/e_2.$$

Thus the primary current behaves in exactly the same manner as in case 1. The secondary-current oscillations, however, occur about a linear axis given by equation (10). After the oscillations have been completely damped out, the secondary current continues to decay to zero along this line, the slope of which is given by $- e_2/L_2$. The total duration of the secondary discharge is Mi_0/e_2. It would appear, therefore, that with high primary currents and small gap-widths which give low values of e_2 the secondary discharge should continue for a considerable time after the oscillations have been damped out and the primary current has fallen to zero.

The above equations appear at first sight to indicate that i_2, after falling to zero, rises again in the reverse direction and eventually reaches an infinite value, while the primary voltage remains constant indefinitely at the value ne_2. It must be recalled, however, that the condition

$$e_2 = \text{constant}$$

applies only so long as i_2 has a positive value. Hence, as soon as i_2 falls to zero the equations no longer hold. At this point the primary voltage, starting at the value ne_2, executes a series of oscillations of small amplitude and of a frequency corresponding to that of the coil with an open secondary and at the same time induces oscillations of small amplitude in the circuit of the secondary and its associated self-capacity.

The above equations thus account satisfactorily for the form of the primary and secondary (current, time) traces obtained with the cathode-ray oscillograph. They show, in particular, that the secondary current, though oscillatory, flows in one direction throughout the life of the discharge and has a duration which is long compared with the natural period of the system. They also show that throughout the greater portion of the discharge the primary current is zero.

§ 3. APPARATUS

The following apparatus was employed:—

(i) An ignition coil, consisting of an m-shaped laminated stalloy core; a primary of 143 turns of no. 24-s.w.g. double-silk-covered copper wire wound in two layers on a cylindrical cardboard former 2·5 cm. in diameter; and a secondary of 10,000 turns of no. 24-s.w.g. enamelled copper wire wound on a former in 35 layers of 420 turns each and separated by waxed tissue paper. In the built-up coil, which could be readily taken apart, the primary with the secondary over it was placed over the middle limb of the core, the latter having a cross-section 1·5 cm. square. In what follows this coil will be referred to as "the coil," or as "the ignition coil."

(ii) A calibrated bank of condensers having mica dielectric and low-resistance conductors. The following capacities and any parallel combination thereof were available: 0·0577, 0·117, 0·237, 0·456, 0·90, and 1·79 μF.

(iii) A make-and-break commutator, with tungsten points, similar to that usually employed in internal-combustion-engine coil-ignition practice. This break, together with certain modifications carried out at a later stage, will be described in further detail below.

(iv) An Ardenne cathode-ray oscillograph and a quarter-plate camera fitted with a Ross Xpres f/1·9 lens.

(v) The time base previously described*.

(vi) A Cambridge triple-element oscillograph with one electrostatic and two electromagnetic elements.

§ 4. DETERMINATION OF THE COIL CONSTANTS

The constants of the built-up coil described above were measured by cathode-ray oscillographical methods similar in most respects to those described by Taylor-Jones† who, however, used an electrostatic oscillograph of special construction.

The chief constants required were the primary inductance and capacity, the secondary inductance and its distributed self-capacity, and the coefficient of coupling. The primary and secondary inductances of the assembled coil were measured on a Campbell inductometer, and also by means of a frequency-meter, at 2000 ~. The coupling was obtained by the method employed by Taylor-Jones† from the relation $n_1^2/n_2^2 = (1 - \kappa^2)$ where n_1 and n_2 were the frequencies of the secondary with the primary circuit open and closed respectively.

n_1, n_2

The following values for the principal coil constants were obtained:—

Primary inductance $L_1 =$ 0·00506 H.,
Secondary inductance $L_2 =$ 11·6 H.,
Coefficient of coupling $\kappa =$ 0·95.

---

* *Proc. Phys. Soc.* **43**, 502 (1931).

† *Loc. cit.*

§ 5. QUANTITATIVE VERIFICATION OF THE THEORY

Case 1. It was not practicable to obtain cathode-ray oscillograms of the secondary current when the secondary was short circuited. A 3040-Ω. resistance connected across the secondary sufficed, however, to provide the voltage necessary to operate the oscillograph satisfactorily.

An oscillogram typical of those obtained is shown in figure 3. The method of measurement has been previously outlined*, the accuracy attained being of the order of 2 per cent. In figure 3 the height of the mean line about which the initial oscillations occur is 23·1 mA., and the height of the first peak above this line is 19·6 mA. The logarithmic decrement of the damped oscillations is 0·16. Therefore, the superimposed exponential decay curve due to the secondary resistance being neglected, the equation to this curve is

$$i_2 = 23{\cdot}1 - 22{\cdot}7e^{-0{\cdot}18\,\omega t/\pi}\cos\omega t,$$

where i_2 is measured in milliamperes. In this case, the primary capacity and current were 0·237 μF. and 1·8 A. respectively. Similar results were obtained for different values of primary capacity, the current at break, however, being kept constant at 1·8 A. The results are summarized in table 1.

Table 1

C_1 (μF.)	A (mA.)	B (mA.)	λ
0·237	23·1	22·7	0·16
0·456	22·9	23·6	0·17
0·900	23·3	24·7	0·23
1·79	22·3	24·3	0·27

A, *B* The constants A and B refer to the general equation to the secondary current

$$i_2 = A - Be^{-\lambda\,\omega t/\pi}\cos\omega t,$$

λ and λ is the logarithmic decrement of the damped oscillations.

From the above results it may be concluded that the secondary current is independent of the primary capacity. According to the theory, the values of A and B should each be equal to ni_0, where $n = \kappa\,(L_1/L_2)^{\frac{1}{2}}$. On substituting the values of κ, L_1 and L_2, it is found that $n = 0{\cdot}02$ when $i_0 = 1{\cdot}8$ A. Hence $ni_0 = 36$ mA., a value which is considerably greater than the mean values of A and B, namely 23 mA. and 24 mA., actually measured in the case of the example under consideration. This, however, is not surprising, because the resistance of the secondary circuit was neglected in the theoretical treatment and in the practical case comprised not only that of the secondary winding itself, but also that of the 3040-Ω. shunt resistance which was required in order to obtain the potential necessary to operate the oscillograph.

It will be seen from table 1 that for small capacities the values of A and B are approximately equal, and that as the capacity is increased the value of A remains approximately constant whilst the value of B increases steadily. This effect is evidently due to the fact that, owing to the presence of resistance in the secondary circuit, the damped oscillations occur about an exponential decay curve instead of about a horizontal straight line. As the capacity is increased the frequency of the oscillations likewise increases, and the first peak moves to a more steeply sloping part of the exponential decay curve. The value of B, which is determined by the height of the first peak, therefore tends to its theoretical value of 36 mA., but the value of A which is determined by the remainder of the oscillations remains constant.

---

* *Proc. Phys. Soc.* **44**, 190 (1932); **43**, 502 (1931).

Case 2. A series of (secondary current, time) oscillograms for various values of gap-widths was obtained. A typical result is shown in figure 4, from which it is clear that the axis of the oscillations, instead of being nearly horizontal as in case 1, is now a steeply sloping straight line (figure 4). For this reason the method* hitherto adopted for measuring the amplitudes of successive oscillations had to be somewhat modified, as follows:—

Let $a_1, a_2, a_3, \ldots$ be the amplitudes of successive oscillations, as measured from the axis. Let p be the constant vertical distance fallen by the axis in half a period. Then, if A_1 is the measured vertical distance between the first and second peaks, A_2 that between the second and third peaks, etc., we have

a_1, a_2, a_3
p
A_1
A_2

$$A_1 = a_1 + a_2 + p,$$

$$A_2 = a_2 + a_3 - p,$$

$$A_3 = a_3 + a_4 + p, \text{ etc.,}$$

or

$$A_1 = a_1(1 + l) + p,$$

$$A_2 = a_1 l(1 + l) - p, \text{ etc.,}$$

where $1/l$ is the decrement,

l

i.e.

$$1/l = (A_1 - A_2)/(A_2 + A_3),$$

and

$$a_1 = (A_1 + A_2)/(1 + l)^2.$$

The linearity of the axis of oscillation was well established by the close agreement between the values of the ratio l found after measuring up each oscillogram. As an example, it will suffice to give the results obtained from one oscillogram (no. 2, 3/6/31). The gap-width was 0·004 in., and the gap was between needle-points in air at atmospheric pressure. The primary current was 1·5 A., and the primary capacity 0·456 μF. The measured amplitudes were as shown in table 2.

The value obtained for a_1 is 23·9 mA., and the logarithmic decrement

$$\lambda = \log(1/l) = 0{\cdot}173.$$

The value for the initial amplitude, corrected for damping, is therefore 28·4 mA. The theoretical value for the initial amplitude is given by ni_0 and is 30 mA.

The oscillation-frequency was found by measurement to be 10,750 ~, the value calculated from the theory being 10,500 ~.

---

* See also § 9.

Table 2

m	A_m (mA.)	$A_m + A_{m+1}$ (mA.)	$1/l$
1	46	81	1·208
2	35	67	1·175
3	32	57	1·186
4	25	48	1·185
5	23	40·5	1·190
6	17·5	34	1·192
7	16·5	28·5	1·187
8	12	24	1·200
9	12	20	1·210
10	8	16·5	1·178
11	8·5	14	1·166
12	5·5	12	—
13	6·5	—	—
Mean value of $1/l$			1·189

The total duration of the discharge was found to be 1·23 msec. Now the total duration is given by the theory as

$$\tau = Mi_0/e_2 = nL_2 i_0/e_2.$$

Therefore

$$e_2 = nL_2 i_0/\tau.$$

Inserting the values $n = 0{\cdot}02$, $L_2 = 11{\cdot}6$ H., $i_0 = 1{\cdot}5$ A., we arrive at a theoretical value for e_2 of 283 V., as compared with a steady value of 295 V. found oscillographically.

Similar oscillograms were taken for various gap-widths, but for similar values of primary capacity and current at break. The results are given in table 3.

Table 3

Gap-width (in.)	Height of first peak (mm.)	τ (msec.)	e_2 calculated (V.)
0	56	—	—
0·004	51·5	1·2	290
0·008	53	1·1	316
0·015	56	0·86	405

It will be seen from the table that on opening the gap a sudden drop occurs in the height of the first peak of the secondary current. As the gap-width is further increased, however, the height of the first peak also increases. This observation is in accordance with the theory outlined above, since

$$i_2 = ni_0 - e_2 t/L_2 - n\,(i_0^2 + I^2)^{\frac{1}{2}}\, e^{-\alpha t/2} \cos(\omega t - \phi).$$

The amplitude of the oscillatory part of i_2 therefore includes the term I where

$$I = \{2\,(ne_2 - e_0) - R_1 i_0\}/2\omega L_1\,(1 - \kappa^2)$$

which increases with e_2.

It is also clear from table 3 that the total duration τ of the discharge decreases with increase in gap-width. This is in accordance with the expression,

$$\tau = ni_0 L_2/e_2,$$

derived above.

Case 3. We may further briefly consider the case in which the breakdown potential of the spark-gap is comparable with the maximum sparking potential afforded by the coil when supplied with a given primary current. In this case the theory outlined above is no longer valid.

Figure 6 *b* shows the (current, time) trace obtained with a primary current of 1·5 A., a primary capacity of 1·79μF. and a gap-width of 0·008 in. The spark is now seen to consist of a series of separate discharges. In this particular example, the series is limited to three distinct discharges, all taking place in the same direction, and each being extinguished before the following one starts. The change from the discharge under the conditions of case 2 to this type of discharge was always found to take place suddenly whenever the primary current was reduced below a certain critical value depending upon the gap-width and frequency.

A feature of considerable interest, plainly visible in figure 6 *b* and also evident on the first half-oscillations of figure 4 and figure 6 *a*, is that a harmonic of small amplitude, low damping and high frequency is superimposed on the main oscillation in each case. Under the conditions of case 2, this harmonic is invariably present but is usually damped out before completion of the first half-cycle. Under the conditions of case 3 where the whole spark in effect consists of a series of discharges, one corresponding with each cycle, the harmonic is invariably prominent in the first half of each cycle and sometimes persists throughout the whole cycle, according to the conditions of primary current and gap-width. We have never been able to observe any trace of this harmonic when the secondary has been shunted by the 3040-Ω. resistance. The frequency of the harmonic is independent of changes in the primary circuit, but its amplitude increases with the gap-width. From the above observations we conclude that these oscillations are in some manner intimately associated with the nature of the spark discharge itself.

Figures 7 *a*, 7 *b* and 7 *c* show oscillograms in which the first (current, time) oscillations, obtained under the conditions of case 1, case 2 and case 3 respectively, are greatly extended in order to show the subsidiary oscillations more clearly. It will be seen that in case 1 no subsidiary oscillations occur and that in case 3 the wave-form of the subsidiary oscillations is distinctly saw-toothed.

§ 6. THE CAPACITY COMPONENT

The capacity component of the discharge has so far eluded direct observation by means of the cathode-ray oscillograph employed in this investigation, on account of its extremely high frequency and currents. Its existence and order of magnitude have, however, been determined indirectly. By making use of a short-wave receiver we found that, in the case of one particular arrangement of secondary leads and spark-gap, the most prominent frequency of the capacity-component oscillations was of the order of 10^7 ~, though several disturbances of both higher and lower frequencies could be detected.

The oscillograms reproduced in figures 2 and 4 afford indirect evidence of the existence and nature of the capacity component. Thus in figures 2 *a* and 2 *b* the secondary-voltage trace is seen to rise rapidly to a maximum value corresponding to the breakdown potential of the gap, whereupon it falls with such extraordinary rapidity to the much lower constant value e_2, pertaining to the inductance component, that throughout this fall the trace is completely invisible. Further, it will be seen that in every case the (current, time) traces obtained under the conditions of case 2 are never seen to start from the origin. A gap invariably exists between the base line and the first visible part of the (current, time) trace. This gap, when observed visually, is seen to increase if the gap-width is increased.

From the general orders of magnitude of the capacities and inductances in the secondary circuit and the extremely high frequency of the capacity-component oscillations, it is evident that the oscillations are set up mainly in the circuit comprising the spark-gap S and the self-capacity C_2 of the secondary circuit including the leads. The initial amplitude of the current oscillations will therefore be given
V, p by VC_2p, where V is the breakdown potential of the gap, p is the pulsatance of the
C_2 oscillations and C_2 is the self-capacity of the coil and leads. Assuming values of $10^{-4}\mu$F. for C_2, 15,000 V. for V and 12×10^6 ~ for the frequency, we obtain a value of 113 A. for the initial current amplitude, a value which is far in excess of the peak-current values of the order of between 10 and 100 mA. characteristic of the inductive component of the discharge. Because of this excessive amplitude and the high frequency of the oscillations, no record of this part of the discharge is seen on the oscillogram. Moreover, whilst the capacity component of the discharge is occurring, the inductive component of the current is steadily increasing from zero; and although it is swamped by the capacity component and so records no trace during that stage of the discharge yet, by the time when the capacity component has been damped out, the inductive component has grown to a small finite value. A gap is therefore seen between the first point in the trace and the base line. The length of this gap is proportional to V, the breakdown potential of the spark-gap, and therefore increases with the gap-width.

§ 7. CONTROL OF THE CAPACITY COMPONENT

The energy of the capacity component is determined solely by the self-capacity of the secondary circuit and the breakdown potential of the gap, i.e. the gap-width, and can therefore be easily varied over a wide range. Its frequency can also be controlled by the inclusion of further inductance in the secondary circuit. Practically complete elimination of the capacity component can be effected by including in the secondary circuit either a suitable resistance or, preferably, a diode run under such conditions as virtually to block the cap acity component whilst passing the inductance component unimpaired.

A discharge in which the capacity component alone occurs, and from which the inductance component is completely absent, must necessarily be obtained when the primary current at break has the least value capable of producing a spark at the gap. A further method of completely eliminating the inductance component without affecting the capacity component is given below.

§ 8. CONTROL OF THE INDUCTANCE COMPONENT

The inductance component of the discharge has been shown to consist of a damped oscillatory current superimposed upon a linearly decaying current. The magnitude and duration of the inductance component are, as we have already seen, nearly directly proportional to the primary current at break and can, therefore, be readily controlled by adjusting the primary current. The inductance component can be completely eliminated, as indicated above, by adjusting the primary current to the least value necessary to produce a spark. The frequency of the oscillations can be controlled by varying the primary capacity. The logarithmic decrement, and with it the amplitude of the first inductance-component oscillation, can be varied by varying the resistance of the primary *LC* circuit.

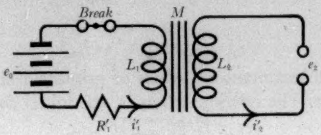


Figure 8.

It now remains to find a means of eliminating portions of the inductance component without affecting the remainder of the discharge. It might be desirable, for example, to examine the ignition properties of the first peak only of the discharge.

Suppose the primary circuit be first broken, thus producing a discharge in the secondary, and then closed again at some instant before cessation of the secondary discharge. The circuit conditions are then as shown in figure 8. The circuit equations are

$$L_1 di_1'/dt + M di_2'/dt + R_1' i_1' - e_0 = 0,$$

and

$$L_2 di_2'/dt + M di_1'/dt + c_2 = 0,$$

where i_1' and i_2' are the primary and secondary currents at any time after the closing of the primary circuit, and R_1' is the primary circuit resistance. These equations may be written in the form i_1', i_2' R_1'

$$(L_1 D + R_1') i_1' + M D i_2' = e_0 \qquad \text{......(10}a\text{)},$$

and

$$M D i_1' + L_2 D i_2' = - e_2 \qquad \text{......(10}b\text{)}.$$

Eliminating i_1' and putting $M^2 = \kappa^2 L_1 L_2$, we obtain

$$[D(D + a')/\{1 - (Me_0 + L_1 e_2) D/R_1' e_2\}]\, i_2' = - a' e_2/L_2,$$

where $a' = R_1'/L_1(1 - \kappa^2)$. a'

The complete solution for i_2' is, therefore,

$$i_2' = A - e_2t/L_2 + Be^{-a't},$$

A, B where A and B are arbitrary constants.

Similarly, eliminating i_2' from equations (10a) and (10b) and substituting M^2 for $\kappa^2L_1L_2$, we obtain

$$(D + a')\, i_1' = (e_0 + ne_2)\, a'/R_1'.$$

The complete solution for i_1' is, therefore,

$$i_1' = (e_0 + ne_2)/R_1' + Ce^{-a't},$$

C where C is an arbitrary constant.

The solutions to the original differential equations are thus

$$i_1' = (e_0 + ne_2)/R_1' + Ce^{-a't} \qquad \text{......(11}a\text{)},$$

and

$$i_2' = A - e_2t/L_2 + Be^{-a't} \qquad \text{......(11}b\text{)}.$$

By substituting these expressions in the original differential equations, the following relation between the three arbitrary constants is obtained:—

$$B + nC = 0 \qquad \text{......(12}a\text{)}.$$

The remaining two relations are obtained from the initial conditions which are that, when $t = 0$,

$$i_1' = i_1 \text{ and } i_2' = i_2,$$

i_1, i_2 where i_1 and i_2 are the instantaneous values of primary and secondary currents at the moment of remake. The relations given by the initial conditions are

$$C + (e_0 + ne_2)/R_1' = i_1 \qquad \text{......(12}b\text{)},$$

and

$$A + B = i_2 \qquad \text{......(12}c\text{)}.$$

The three equations, (12a) to (12c), determine the arbitrary constants as follows:—

$$A = i_2 + ni_1 - n\,(e_0 + ne_2)/R_1',$$

$$B = n\,(e_0 + ne_2)/R_1' - ni_1,$$

and

$$C = i_1 - (e_0 + ne_2)/R_1'.$$

On substitution of the above values for the arbitrary constants, equations (11a) and (11b) become

$$i_1' = (1 - e^{-a't})\,(e_0 + ne_2)/R_1' + i_1e^{-a't} \qquad \text{......(13}a\text{)},$$

and

$$i_2' = (1 - e^{-a't})\,\{i_1 - (e_0 + ne_2)\}\, n/R_1' + i_2 - e_2t/L_2 \qquad \text{......(13}b\text{)}.$$

If the primary circuit be closed when the oscillations have been damped out, or at a moment when the primary and secondary currents are passing through their mean values, then $i_1 = 0$, in which case

$$i_1' = (1 - e^{-a't})\,(e_0 + ne_2)/R_1' \qquad \text{......(14}a\text{)},$$

and

$$i_2' = i_2 - e_2t/L_2 - n\,(1 - e^{-a't})\,(e_0 + ne_2)/R_1' \qquad \text{......(14}b\text{)}.$$

Thus the secondary current falls rapidly to zero at the moment of re-establishment of the primary circuit. The term e_2t/L_2, which represents the slow rate of fall of the secondary current obtained when the primary circuit is left open, is negligible in all practical cases in comparison with the exponential term, and we can write, therefore,

$$i_1' = (i_0 + ne_2/R_1')(1 - e^{-a't}) \qquad \text{......(15}a\text{)},$$

and

$$i_2' = i_2 - n(i_0 + ne_2/R_1')(1 - e^{-a't}) \qquad \text{......(15}b\text{)},$$

because $i_0 = e_0/R_1'$.

Since i_2 can never be greater than ni_0, the term $n(i_0 + ne_2/R_1')$ is always greater than i_2. The secondary current therefore reaches zero after a finite time. Suppose that after interruption the primary circuit be re-established at a time equal to half the normal duration of the discharge, and that the oscillations have either been damped out before this point is reached or the primary and secondary currents are passing through mean values. Then,

$$i_2 = ni_0/2 \quad \text{and} \quad i_1 = 0.$$

Therefore

$$i_2' = ni_0/2 - n(i_0 + ne_2/R_1')(1 - e^{-a't}).$$

When $i_2' = 0$,

$$e^{a't} = (i_0 + ne_2/R_1')/(i_0/2 + ne_2/R_1').$$

Assuming the following values,

$$n = 0{\cdot}02,$$
$$i_0 = 2 \text{ A.},$$
$$e_2 = 360 \text{ V.},$$
$$R_1' = 3\ \Omega.,$$
$$L = 0{\cdot}005 \text{ H.},$$

and

$$\kappa = 0{\cdot}95,$$

then the value deduced for t is $48\,\mu$sec. When the primary circuit is left open throughout the life of the discharge, then the time taken for the secondary current to fall to zero is given by $t = ni_0L_2/2e_2$. Assuming the value of 11·6 H. for L_2, the value obtained for t is $650\,\mu$sec., a value which is 14 times that in the previous case where the primary circuit was closed during the life of the secondary discharge.

When it is remembered that, in calculating the duration of the secondary current after re-establishment of the primary circuit, the term e_2t/L_2 was neglected, and also that the decay of the secondary current occurs along an exponential curve, it becomes evident that an extremely rapid interruption of the secondary current should be obtainable.

A similar effect may be predicted to occur if remake, i.e. closing of the primary circuit, takes place at any other point along the secondary-current curve. If, for instance, remake be effected at the peak of an oscillation in the inductance component, then values of i_1 and i_2 can be readily calculated and the equation for i_2' found in the manner indicated above. In every case an equation is obtained which indicates that on remake the secondary current decays rapidly to zero in a time which is short in comparison with the total normal life of the discharge.

The total duration of the secondary discharge, which depends upon the value of i_0, under normal working conditions seldom exceeds 2 msec. Thus, in order to test the above conclusions, it was necessary to have some form of contact-breaker which could be made to close after break in such a manner that the time during which the primary circuit was open could be continuously varied with sufficient precision over the range between 0 and, say, 4 msec. A first attempt to obtain this effect, by varying the maximum opening of the breaker contacts, failed as a result of irregular arcing due to the extremely small opening necessary. A second attempt, by recutting the contact-breaker cam surfaces, likewise proved unavailing because, owing to the exceedingly steep cam-surface angles required, it was not found possible to make the contact arm follow the cam throughout its travel.

Finally, the type of contact-breaker* described below and shown diagrammatically in figure 9 was evolved with satisfactory results.

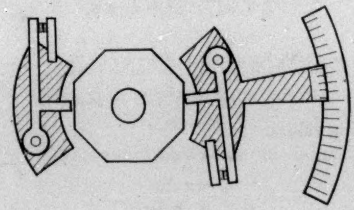


Figure 9.

The two pairs of contacts are shown on opposite sides of the cam. In practice they are arranged one above the other on the same side of the cam.

Two pairs of contacts in parallel were connected in the primary circuit. One pair of contacts was fixed in relation to the axis of an octagonal cam, about which the second pair could be rotated and secured in any required position. The angle of displacement between the pairs of contacts could be measured by means of an arc and vernier.

The operation of this contact-breaker was as follows. On rotation of the cam, with the moveable contact pair set out of phase with the fixed contact pair, one pair of contacts opened, but the other pair remained closed. The primary circuit was therefore still complete. On further rotation of the cam, the first pair of contacts began to close, but shortly before completion of the closure the second and hitherto closed pair opened, thus breaking the primary circuit which was afterwards remade by the closing of the first contact pair. This device made it possible to obtain any desired time of opening within the limits stated above and proved further to be free from sparking.

The results of some experiments carried out with the new contact-breaker are shown in figures 10 *a* to 10 *e*, in which are seen the effect of various times of opening upon the secondary current. It will be noticed particularly that on re-establishing the primary circuit during the life of the discharge the secondary current drops with great rapidity to zero, as predicted by the theory outlined above. Simultaneously the primary current, as shown by the electromagnetic oscillogram, figure 11, rises rapidly to a definite value and then continues to rise, but at a much slower rate the time constant of which is characteristic of the ordinary type of remake of the primary occurring at any time after the cessation of the secondary discharge. That this is completely in accordance with the theory developed above will be seen if the primary current equations for early remake and for build-up under ordinary conditions are compared. The two equations are, respectively,

---

* B.P. 381,917 (1932).

$$i_1' = (i_0 + ne_2/R_1')\{1 - e^{-R_1't/2L_1(1-\kappa^2)}\},$$

and

$$i_1' = i_0\{1 - e^{-R_1't/2L_1}\}.$$

It will be seen that the rate at which the primary current builds up has been greatly increased. The time constant of the circuit has been reduced from L_1/R_1' to $L_1(1-\kappa^2)/R_1'$, i.e. to about a tenth of its normal value, and the primary current builds up as if approaching a final value of $(i_0 + ne_2/R_1')$ instead of i_0. The former value is clearly never reached in practice because the equations cease to hold as soon as the secondary current has fallen to zero which it does before the primary current has reached the value i_0. Upon complete extinction of the secondary discharge the primary current continues to build up towards its ultimate final value i_0, but at a rate now corresponding to a time constant L_1/R_1'.

Further secondary-current oscillograms were taken under conditions in which the primary circuit was remade at points intermediate between those shown in figures 10 *a* to 10 *e*. In all essentials similar results were obtained, and this shows that remake can be effected at any point on the secondary-current curve, either before, upon or after attainment of the secondary-current peak values, without affecting the essential features outlined above. Thus the value to which the primary current builds up at the rapid rate is independent of the instantaneous value at the moment of remake of the oscillatory component of the secondary current and depends only upon the value of the mean secondary current at the moment of remake

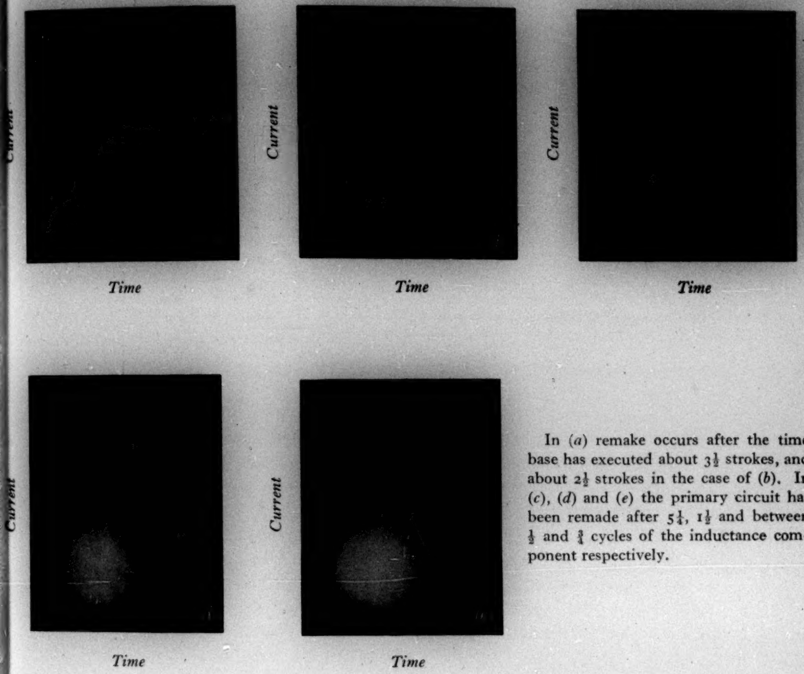
Thus complete control of the secondary discharge characteristics is possible. Those portions of the discharge whose igniting properties require examination can now be isolated. For example, the capacity component may be isolated with great precision by re-establishing the primary circuit at the beginning of the inductance component. Should it be desired to produce a discharge consisting of a single impulse, such as the first half-cycle of the inductance component, the break is set in such a manner that remake occurs at some instant after the first peak, but before the first trough in the inductance component oscillation, the capacity component being absorbed by means of a suitable resistance or diode connected in the secondary circuit.

§9. NOTE ON THE OSCILLOGRAM SHOWN IN FIGURE 5

In this oscillogram the (current, time) trace has been reversed by reversing the polarity of one pair of the oscillograph deflecting plates half-way through the exposure. By this means increased accuracy in the measurement of the oscillogram is obtained.

§ 10. ACKNOWLEDGMENTS

The above investigation was undertaken at the suggestion of the late Dr S. Z. de Ferranti, F.R.S., who was also actively associated with its prosecution until shortly before his death. We wish to place on record our deep sense of appreciation of Dr Ferranti's inspiring influence and of the liberal financial assistance afforded by Messrs Ferranti Ltd., without which the work could not have been carried out.



In (*a*) remake occurs after the time base has executed about 3½ strokes, and about 2½ strokes in the case of (*b*). In (*c*), (*d*) and (*e*) the primary circuit has been remade after 5¼, 1½ and between ½ and ¾ cycles of the inductance component respectively.

Figure 10.

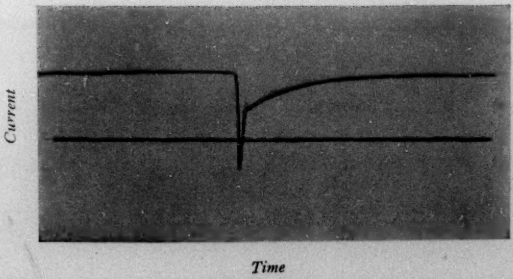


Figure 11.

551.585.1

THE WET-AND-DRY-BULB HYGROMETER: THE RELATION TO THEORY OF THE EXPERIMENTAL RESEARCHES OF AWBERY AND GRIFFITHS

By F. J. W. WHIPPLE, M.A., Sc.D., F.Inst.P.

Received November 23, 1932. *Read January* 20, 1933.

ABSTRACT. Simultaneous values have been published by Awbery and Griffiths of the dew-point, the vapour content as determined by a gravimetric method, and the reading of a wet-bulb thermometer, the observations covering a range of air-temperature from 30° to 100° C.

These observations have been rediscussed and it is demonstrated that August's formula by which vapour-pressure is deduced from dry- and wet-bulb readings is valid over the experimental range of temperature.

§ 1. INTRODUCTION

The wet-and-dry-bulb hygrometer is primarily apparatus for finding the humidity of the air, but it may be regarded also as apparatus for conducting a physical experiment demonstrating the cooling effect of evaporation. The recent paper* by Messrs Awbery and Griffiths, a study of observations of dry- and wet-bulb thermometers immersed in a stream of air and water vapour at temperatures ranging up to 100° C., meets adequately the need for tables by which humidities can be deduced from thermometer readings. The authors say nothing of the theoretical aspect of their observations, but by setting these out in detail they have given an opportunity, to anyone interested, to test such theories as may be suggested.

My examination of the observations leads to the conclusion that, within the order of accuracy of the investigation, the formula originally proposed by August and in general use for computing humidity at ordinary atmospheric temperatures is valid at high temperatures. Short tables of humidities computed by this formula and by a slightly modified formula have been prepared. These new tables may be compared with the final table of the paper by Awbery and Griffiths. As was to be anticipated, the differences between the tables are of no practical importance.

A notable result of the investigation is that at high temperatures very good ventilation of the wet bulb is not essential.

§ 2. AUGUST'S HYPOTHESIS AND THE RESULTING FORMULAE

The theory of the wet-bulb thermometer depends in the first instance on the conditions for equilibrium of the temperature of the thermometer bulb itself. The bulb is cooler than its surroundings. It receives heat from the air but it is also receiving heat by radiation from objects in the neighbourhood, by conduction down the thermometer stem and by the supply of fresh water. To take account of all these factors is practically impossible. All but the first are, however, comparatively unimportant when the air current passing the wet bulb is strong. Under such circumstances the wet bulb may be regarded as merely receiving heat from the air and giving up that heat as the latent heat of evaporation.

---

* *Phys. Soc. Proc.* **44**, 115 (1932).

August's hypothesis* with regard to this exchange is that the air which gives up its heat to the wet bulb and thereby promotes evaporation is identical with the air which receives the evaporated moisture; the air becomes saturated at the wet-bulb temperature. The formula which will represent this hypothesis requires careful consideration if it is to be applied in extreme conditions with vapour pressure comparable with the total atmospheric pressure.

As a preliminary some discussion of latent heat is necessary. The latent heat of evaporation is naturally defined as the heat required to convert so much water into saturated vapour at the same temperature and under the pressure of that vapour alone. It is therefore important to demonstrate that the heat required is the same when the pressure is due to a mixture of air and water vapour.

V, P m, v L, E_1 E_2 J

Let the volume V be occupied by air and vapour at the pressure P. When the additional quantity m of water evaporates the volume is increased to $V+v$. Let mL be the latent heat under these circumstances. Further let mE_1 be the internal energy of the water to be evaporated and mE_2 the energy of the corresponding vapour. If E was the internal energy of the air and the original vapour, then the final value of the internal energy is $E+mE_2$. Further, the work done by the expanding mixture is, in heat units, Pv/J, J being the mechanical equivalent of heat. Accordingly

$$mL = [E + mE_2 + Pv/J] - [E + mE_1],$$

so that

$$mL = m(E_2 - E_1) + Pv/J.$$

P_1

Now if P_1 is, in the final state, the partial pressure of the original air and water vapour, then by Boyle's Law

$$P_1(V+v) = PV.$$

P_2

Further, if P_2 is the partial pressure of the new vapour, $P_1 + P_2 = P$ and hence

$$Pv = P_2(V+v) = R'\theta' m,$$

R', θ'

where R' is the gas constant for water vapour and θ' the temperature at which the process takes place. It follows that

$$L = E_2 - E_1 + R'\theta'/J.$$

Since P does not occur in this equation the value of L is not affected by the presence of the air. I am indebted to Mr D. Brunt for the enunciation and proof of this rule.

---

* It is doubtful whether August contemplated a continuous exchange. He refers to what has happened in the thin layer around the wet bulb. In this layer the air has evidently yielded up its heat to assist in the formation of water vapour. J. D. Everett, *Q.J.R. Met. Soc.* **18**, 13 (1892).

We proceed with the discussion of August's hypothesis. Let

P be the atmospheric pressure;
θ, θ' the dry- and wet-bulb temperatures; θ, θ'
e the vapour pressure of the atmosphere; e
e' the vapour pressure of saturated vapour at the temperature θ'; e'
c the specific heat of dry air at constant pressure; c
c' the specific heat of water vapour at constant pressure; c'
L the latent heat of evaporation at temperature θ'; L
n the ratio of the densities of water vapour and dry air at the same pressure and temperature. n

The hypothesis under consideration is that a certain sample of air, initially at temperature θ and pressure P and containing sufficient water vapour to exert a pressure e, is diluted with more water vapour; the mixture is at temperature θ' and pressure P, and contains sufficient water vapour to exert a pressure e'. The loss of heat is exactly balanced by the latent heat of evaporation of the additional vapour. Let M be the mass of dry air in the sample. The mass of vapour was initially $Mne/(P-e)$. In the final state the mass of vapour associated with M is $Mne'/(P-e')$. The additional quantity of water vapour is therefore m, where M

$$m = \left(\frac{e'}{P-e'} - \frac{e}{P-e}\right) Mn = \frac{P(e'-e)}{(P-e)(P-e')} Mn.$$

The exchange of heat is equivalent to that taking place in the following stages: (1) the original air and water vapour are brought to the temperature θ', the pressure remaining constant; (2) the additional water vapour is evaporated under the pressure P into the atmosphere at the temperature θ'.

By hypothesis the heat communicated to the wet bulb by radiation, etc. is to be ignored. Accordingly the equation of equilibrium is

$$\frac{(e'-e)PnL}{(P-e)(P-e')} = (\theta-\theta')\left[c + \frac{e}{P-e} nc'\right].$$

Since in c.g.s. units $c = 0{\cdot}24$, $c' = 0{\cdot}42$ and $n = 0{\cdot}622$, it follows that $nc'/c = 1{\cdot}09$. As long as e is considerably less than P, the difference between this number 1·09 and unity may be ignored without serious error. With that simplification the equation of equilibrium reduces to

$$e' - e = B_1 P(\theta - \theta'),$$

where $$B_1 = \left(1 - \frac{e'}{P}\right)\frac{c}{nL}.$$ B_1

In the usual and historic statement of the theory the factor $(1 - e'/P)$ does not appear, and the psychrometric equation is then

$$e' - e = B_0 P(\theta - \theta'),$$

where $$B_0 = c/nL.$$ B_0

An expression including a factor equivalent to $(1 - e'/P)$ is given* however by Apjohn, a contemporary of August's.

The distinction between B_0 and B_1 will become very important when the temperature of the wet bulb approaches the boiling-point. Numerical values of B_0 and B_1 are given below (p. 314).

§ 3. TAYLOR'S THEORY

August's hypothesis, at any rate in the explicit form adopted here, is obviously artificial. In reality the air current cannot be divided sharply into two streams, one of which becomes saturated whilst the other is unaffected by the presence of the wet bulb. A more complicated theory, proposed by G. I. Taylor, was communicated by him to Principal Skinner, who published it in the article on humidity in the *Dictionary of Applied Physics*, III (1923). Taylor's hypothesis is that, whilst the air-flow is generally turbulent, there is a film of non-turbulent air passing slowly over the wet bulb. The diffusion of heat and of moisture are of different characters in the turbulent layer and in the non-turbulent film.

θ, e, θ', e'
θ'', e''
z, k
D
ρ

Let θ and e be the temperature and vapour-pressure in the free air; θ' and e' are the values at the surface of the wet bulb; θ'' and e'' are the values at the boundary between the film and the turbulent air. Let z be the thickness of the film, k the conductivity of air and D the diffusivity of water vapour through air. Following Skinner we regard the density of air as a constant ρ. The density of water vapour at pressure e is accordingly $n\rho e/P$.

The rate at which heat is conducted inwards to the wet bulb is per unit area

$$k(\theta'' - \theta')/z.$$

The rate at which water vapour diffuses outwards from the density $n\rho e'/P$ to the density $n\rho e''/P$ is

$$Dn\rho(e' - e'')/Pz.$$

As the incoming heat evaporates the water,

$$k(\theta'' - \theta') = Dn\rho(e' - e'')L/P.$$

E

Now let E be the rate at which eddies are replacing the cool damp air of the outside of the film by the warmer, drier, natural air. E is reckoned as volume per unit area and unit time.

The rate at which heat is carried inwards is

$$E\rho c(\theta - \theta'').$$

The rate at which water vapour is carried outwards is

$$En\rho(e'' - e)/P.$$

The physical significance of E is rather vague; the essential assumption is that the coefficient E has the same value in both these statements.

Since the flow of heat inwards and of water vapour outwards are both continuous, it follows that

$$E\rho c(\theta - \theta'') = En\rho(e'' - e)L/P.$$

Thus

$$e'' - e = P(\theta - \theta'')c/nL,$$

---

* *B.A. Report* 1843, p. 36.

whilst
$$e' - e'' = \frac{P(\theta'' - \theta')}{nL} \frac{k}{\rho D}.$$

To eliminate e'' and θ'' simultaneously between these last two equations is only possible if
$$c = k/\rho D.$$

Now it so happens that
$$k/\rho D = 0{\cdot}22,$$

whilst
$$c = 0{\cdot}24.$$

The quoted values of k, ρ and D refer to the temperature 0° C., but it is known that $k/\rho D$ is nearly independent of temperature. We may ignore the difference between 0·22 and 0·24 and so obtain the equation
$$e' - e = B_0 P(\theta - \theta')$$
with $B_0 = c/nL$ as before.

According to Taylor dry-and-wet-bulb hygrometry is possible only because the diffusivity of water vapour through air and the conductivity of air are related in such a special way. Otherwise under varying conditions the changes in temperature and humidity in the eddy layer and in the non-turbulent layer would not be in proportion and there would not be a definite wet-bulb temperature corresponding with a given hygrometric state of the air.

It is possible to analyse more closely the details of Taylor's theory. For instance we can take account of the continual displacement of water from the outside of the non-turbulent film and regard θ'' and e'' as averages. We can investigate the diffusion of vapour through the film and allow for the fact that the gradient is not uniform. The gradient of temperature is also not uniform. Further we might allow for the fact that the density of the air is not constant. The general result of all these refinements is that the psychrometric formula with the constant B_0 is not exact and that the formula involving B_1 is likely to be nearer to the truth.

Experiments with water on the wet bulb in the ordinary atmosphere will not enable us to discriminate between August's theory and Taylor's. By the use of other liquids and gases it has been demonstrated that Taylor's is the more satisfactory.

§ 4. THE EXPERIMENTS OF AWBERY AND GRIFFITHS

Awbery and Griffiths exposed their dry- and wet-bulb thermometers in a current of humidified air at atmospheric pressure. They determined the humidity in two ways, by the dew-point and by a gravimetric method. They give their results as relative humidities corresponding with given readings of the dry- and wet-bulb thermometers. For comparison with theory we require the vapour pressure. The method of reduction may be illustrated by the first entries in table 1 of the paper*.

---

* The vapour pressures are taken from the *Wärmetabellen* of Holborn, Scheel and Henning (Braunschweig, 1919).

Dry-bulb temperature $= \theta = 100{\cdot}6^\circ$ C.
Wet-bulb temperature $= \theta' = 75{\cdot}0^\circ$ C.
Relative humidity by dew-point method $= r_1 = 35{\cdot}3\ \%$.
,, ,, by gravimetric method $= r_2 = 35{\cdot}6\ \%$.
Saturation pressure at temperature θ $= E = 776{\cdot}4$ mm.
Vapour pressure by dew-point method $= e_1 = r_1 E = 274$ mm.
,, ,, by gravimetric method $= e_2 = r_2 E = 276$ mm.
,, ,, over wet bulb $= e' = 289$ mm.

We require the coefficient B in the formula

$$e' - e = BP\,(\theta - \theta').$$

Assuming $P = 760$ mm. and substituting from the foregoing data, we find:

B_d By dew-point method $B_d = 8 \times 10^{-4}$.
B_g By gravimetric method $B_g = 7 \times 10^{-4}$.

The estimates of B_d and of B_g are plotted in figures 1 and 2 respectively, the co-ordinates being θ' and $(\theta - \theta')$. A few anomalous results have not been plotted. It will be seen that there is no very systematic distribution of the entries. B_d tends to be small when $(\theta - \theta')$ is small and θ' is high, but there is no similar tendency with B_g.

The estimates exceeding 9×10^{-4} and less than 2×10^{-4} happen to be equally numerous. When these are excluded the mean values of B_d and B_g are $6{\cdot}3 \times 10^{-4}$ and $6{\cdot}9 \times 10^{-4}$ respectively.

It follows that the observations as a whole can be represented by the formula

$$e' - e = BP\,(\theta - \theta')$$

with

$$B = 6{\cdot}6 \times 10^{-4},$$

but the question whether B is really constant must be left open.

It is remarkable that whilst the observations of Awbery and Griffiths yield such good curves when plotted in their paper with relative humidity and dry-bulb temperature as variables, the same observations give the irregular distribution of numbers in figures 1 and 2. The reason is that the wet-bulb temperature and the dew-point differ but slightly, so that a small error in either, an error which hardly affects the relative humidity, has a large influence on B, the variable of the present paper. In the example cited above if the distinction between wet-bulb temperature and dew-point had been ignored the relative humidity would have been computed from the wet-bulb reading as e'/E or 37 per cent. As the true value was 35 per cent the error would for most purposes have been negligible.

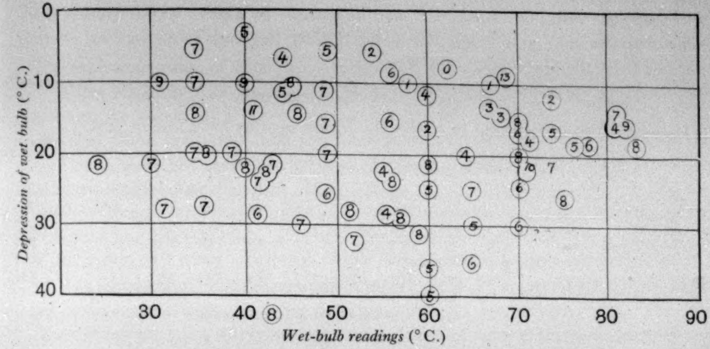


Figure 1. Values of $10^4 B$ as determined by dew-point observations.

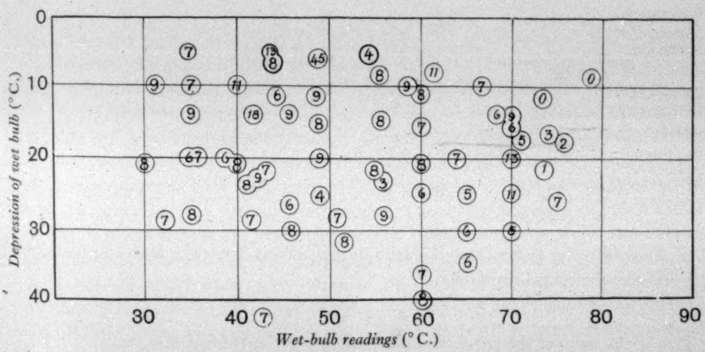


Figure 2. Values of $10^4 B$ as determined by absorption method.

§ 5. THEORY AND EXPERIMENT

To sum up the results, I have set out in table 1 the values of the coefficient B given by theory and by observation and also those adopted in certain tables.

The theoretical values are those given by the formulae for B_0 and B_1 in the present paper. The values adopted* for the latent heat are Henning's†. The best set of outdoor experiments for deriving the coefficient B is that made by Prof.

---

* The values of latent heat used by August, Apjohn and Regnault are quoted by Everett, *Q.J.R. Met. Soc.* **18** (1892). All used 0·267 for *c*.

† *Wärmetabellen*, p. 67, quoting from *Ann. d. Phys.* **29**, 441 (1909).

Marvin and other observers in the United States, some at considerable altitudes and therefore with low values of P, and discussed* by Prof. Ferrel. Marvin used sling thermometers and found the dew-point by Regnault's hygrometer. Ferrel derived from the observations the formula

$$B = 6{\cdot}56 \times 10^{-4} (1 + {\cdot}0019\theta').$$

This formula has been used to obtain the results against his name in table 1.

Table 1. The psychrometric constant, in theory and in practice

Temperature (° C.)	0	10	20	30	40	50	60	70	80	90	100
of wet bulb (° K.)	273	283	293	303	313	323	333	343	353	363	373
Vapour pressure (mm.)	4·6	9·2	17·5	31·8	55	93	149	234	355	526	760
(mb.)	6·1	12·3	23·4	42·5	74	123	199	312	473	701	1013
Latent heat (cal./gm.)	595	590	585	580	575	569	563	558	552	545	539
					Values of B (c.g.s. units × 10^{-4})						
Theory:											
B_0 or c/nL	6·49	6·54	6·60	6·66	6·72	6·79	6·86	6·92	7·00	7·08	7·16
B_1 or $(1 - e'/P)\,B_0$	6·45	6·46	6·45	6·38	6·23	5·97	5·52	4·79	3·73	2·19	0·00
Observation:											
Marvin-Ferrel	6·56	6·68	6·81	6·93	—	—	—	—	—	—	—
Svennson	←—	6·45	—→	—	—	—	—	—	—	—	—
Awbery and Griffiths:											
Dew-point	—	—	—	←—	——	6·3	——	—→	—	—	—
Gravimetric	—	—	—	←—	——	6·9	—→	—	—	—	—
Tables:											
Smithsonian (Ferrel)	6·60	6·68	6·75	6·83	—	—	—	—	—	—	—
Assmann (Sprung)	←—	——	6·62	—→	—	—	—	—	—	—	—
Accompanying tables 2, 3	—	—	—	←—	——	6·6	——	——	——	——	—→

Note. The theoretical values of B are found on the assumptions that $c = 0{\cdot}24$, $n = 0{\cdot}622$.

Accepting the theory that B ought to vary inversely as the latent heat, Ferrel found the alternative formula

$$B = 6{\cdot}60 \times 10^{-4} (1 + {\cdot}00115\theta').$$

This is the basis of the psychrometric tables† used in the United States.

Of laboratory experiments the best known are those of Svennson‡ who aspirated air past his thermometers in a vessel in which the air-pressure was sometimes reduced as low as 300 mm. The vapour pressure was determined by Sonden's apparatus in which the actual vapour pressure of a sample of the atmosphere can be measured directly. Svennson's value of B is lower than that adopted by most observers. He considers that this is because there are systematic errors in dew-point determinations and in the absorption method. These tend to give too low values for e. It will be noticed that Svennson's value of B is in good agreement with our formula for B_1.

---

* *Annual Report, Chief Signal Officer, Washington*, App. 24 (1886).

† *Smithsonian Meteorological Tables*, tables 82, 84 (5th Edition, 1931).

‡ *Met. Z.* **13**, 201 (1896).

The tables adopted* for the Assmann psychrometer are based on the simple formula given by Sprung†

$$e' - e = 0{\cdot}5\,(\theta - \theta')\,P/755.$$

The equivalent value of B is $6{\cdot}62 \times 10^{-4}$.

There has been some tendency in the past to lay undue stress on the differences between the values of B given by one investigator and another and to say that empirical tables are better than any formula for deriving humidity from wet-bulb readings. As will be seen from table 1, the range of values of the coefficient B for ordinary temperatures is quite small. There is, it is admitted, considerable uncertainty about the best use to be made of the readings of wet-bulb thermometers which are not "well ventilated" but that uncertainty need not affect confidence in the interpretation of the readings of such thermometers as *are* well ventilated.

It is satisfactory that the new determinations of B for moderate temperatures are in agreement with the older determinations for low temperatures. The new observations are not good enough, however, to discriminate between the merits of the formulae in which the coefficients are B_0 and B_1.

§ 6. NEW TABLES

To cover the range of observations with dry-bulb temperatures up to 100° C., skeleton tables of vapour pressure and relative humidity have been prepared.

Our theoretical discussion led to the conclusion that the coefficient B should be variable and a function of the wet-bulb temperature, whilst the observations were satisfied well enough by the assumption that B was constant. Tables based on each of these hypotheses have been prepared. It might have been anticipated that the tables computed on the two assumptions would be utterly inconsistent. As a matter of fact, the differences are insignificant. The reason is that at high temperatures the difference between the wet-bulb temperature and the dew-point is small, and the results of using alternative values of the factor B cannot be distinguished. Further, the agreement between the tables of relative humidity and that of Awbery and Griffiths is almost perfect. The only discrepancy is where they had extrapolated for wet-bulb depressions beyond the range of experiment.

It is a practical deduction from these comparisons that in psychrometric observations at high temperatures strong ventilation is not a necessity. This must be true, since the computed humidities would be affected but slightly if Regnault's moderate-wind value were used for B, instead of the strong-wind value. On the other hand I should like to express the hope that experiments will be made to fix the values of B more precisely. I would suggest for consideration the use of a differential thermometer to determine the interval between the dew-point and the wet-bulb temperature. If room air were used without the admixture of steam, the experiment would be comparatively easy to control, and consistent values of the psychrometer constant B, accurate to two significant figures, might be obtained.

---

* *Aspirations-Psychrometer-Tafeln* (Braunschweig, 1908).

† *Das Wetter* (1888).

Table 2*. Vapour pressure derived from psychrometer readings by the use of the empirical formula, $B = 6{\cdot}6 \times 10^{-4}$

Dry-bulb temperature (° C.)	30	40	50	60	70	80	90	100
Wet-bulb depression (° C.)	Vapour pressure (mb.)							
0	42·5	73·8	123·3	199	312	473	701	1013
5	28·4	53·0	92·6	154	247	382	575	842
10	16·7	35·8	67·1	117	192	305	467	694
15	7·1	21·7	46·3	86	148	240	375	568
20	—	10·0	29·1	60	110	186	299	460
25	—	0·4	15·0	40	79	141	234	368
30	—	—	3·3	22	54	103	179	292
35	—	—	—	8	33	73	134	227
40	—	—	—	—	16	47	97	172
45	—	—	—	—	2	26	66	127

Table 3*. Relative humidity derived from psychrometer readings by the use of the empirical formula, $B = 6{\cdot}6 \times 10^{-4}$

Dry-bulb temperature (° C.)	30	40	50	60	70	80	90	100
Wet-bulb depression (° C.)	Relative humidity (per cent)							
0	100	100	100	100	100	100	100	100
5	67	72	75	77	79	81	82	83
10	39	49	54	59	62	65	67	69
15	17	29	38	43	47	51	54	56
20	—	14	24	30	35	39	43	45
25	—	1	12	20	25	30	33	36
30	—	—	3	11	17	22	26	29
35	—	—	—	4	11	15	19	22
40	—	—	—	—	5	10	14	17
45	—	—	—	—	1	5	9	13

* Tables 2 and 3 are computed for normal atmospheric pressure; $P = 1013$ mb.

Table 4*. Vapour pressure derived from psychrometer readings by the theoretical formula, $B_1 = (1 - e'/P)\, c/nL$

Dry-bulb temperature (° C.)	30	40	50	60	70	80	90	100
Wet-bulb depression (° C.)	Vapour pressure (mb.)							
0	42·5	73·8	123·3	199	312	473	701	1013
5	28·5	53·1	92·8	155	248	383	576	844
10	16·9	36·0	67·5	117	193	307	469	699
15	7·3	21·9	46·7	87	149	243	379	573
20	—	10·3	29·6	61	111	188	302	465
25	—	0·7	15·4	40	80	143	237	374
30	—	—	3·8	23	55	105	182	297
35	—	—	—	9	34	74	137	232
40	—	—	—	—	17	49	99	177
45	—	—	—	—	2	30	68	131

Table 5*. Relative humidity derived from the values of vapour pressure in table 4

Dry-bulb temperature (° C.)	30	40	50	60	70	80	90	100
Wet-bulb depression (° C.)	Relative humidity (per cent)							
0	100	100	100	100	100	100	100	100
5	67	72	75	78	80	81	82	83
10	40	49	55	59	62	65	67	69
15	17	30	38	44	48	51	54	57
20	—	14	24	31	36	40	43	46
25	—	1	12	20	26	30	34	37
30	—	—	3	12	18	22	26	29
35	—	—	—	5	11	16	20	23
40	—	—	—	—	5	10	14	17
45	—	—	—	—	1	6	10	13

* Tables 4 and 5 are computed for normal atmospheric pressure; $P = 1013$ mb.

DISCUSSION

Dr EZER GRIFFITHS. I am gratified to hear that Dr Whipple has been able to verify the theory of the wet-and-dry-bulb thermometer by means of our experimental observations. It is a very interesting point that the formula holds good over such a wide range of temperature. Has the author considered the case of dry-bulb temperatures below 0° C.? We are engaged at present in a study of hygrometers at low temperatures. In this investigation the wet bulb is covered with a sheath of ice. We use various forms of the wet-and-dry-bulb hygrometer. In some the wet-and-dry bulbs take the form of a differential thermo-element with 33 wet and dry junctions. In others differential resistance thermometers are used. The wet-and-dry-bulb method is compared with the gravimetric and dew-point methods, both of which present considerable experimental difficulties at low temperatures.

Mr J. H. Awbery. I think Dr Griffiths agrees with me in that the wet-and-dry-bulb formula has never seemed to us to be based on a satisfactory theory. Even now, with the improved derivation given by the author of this paper, its basis includes the equality of 0·22 with 0·24; and we have no investigation of the errors which arise by ignoring the difference between these two quantities. Whatever may be the basis of the formula, its practical utility cannot really be denied. I had never compared direct observation with the formula until recently, but the present paper led me to analyse our own results in the light of the equation. I am now completely converted to the view that for smoothing observations it is perfectly satisfactory; but my adherence to orthodoxy is on account of empirical evidence, and is not due to an inward realization of truth.

That my conversion is real, may be inferred from the fact that the detailed table which Dr Griffiths and I have prepared* was constructed in part with the assistance of the formula.

Mr C. S. Wright. I should like to ask Dr Whipple whether meteorologists place any reliance on the readings of wet-and-dry-bulb thermometers in moderately low temperatures? The last Scott Expedition observed a condensation in the winter on ice surfaces, when the wind velocity was low. Kidston in his analysis of the results of Shackleton's first expedition explains the numerous occasions of a *higher* wet-bulb than dry-bulb temperature as due to a similar condensation on the ice surrounding the "wet" bulb. May not condensation also occur above freezing-point?

Author's reply. My answer to Dr Griffith's question is that I see no reason to doubt that a formula of August's type should be valid for the case in which the wet bulb is covered with ice. Meteorologists use different formulae for ice-covered and water-covered bulbs (allowing for the greater latent heat of evaporation from ice) and also recognize the distinction between the vapour pressure of air saturated with respect to ice and to water.

In Observatory practice we find that the wet-bulb thermometer is frequently below the freezing-point for many hours before the water on the muslin freezes. Moreover freezing takes a considerable time, and so does thawing. On account of uncertainties as to the state of the covering of the wet bulb, it is found better to trust to the hair hygrograph for finding humidity of air near the freezing-point.

For finding humidities at the low temperatures encountered in aeroplane ascents the Meteorological Office provides observers with warm water in a thermos flask. Between observations the wet bulb is dipped into the water and a new coating of ice is soon formed.

---

* *National Physical Laboratory, Annual Report for* 1932.

No satisfactory method has been evolved for determining the humidity at great heights—for example, in the stratosphere, where temperature is comparable with 220° K. Saturation pressure at that temperature is only 0·027 mb. as compared with 6·1 mb. at the freezing-point. I hope that Messrs Awbery and Griffiths will be able to make some practical suggestion. We want to know more about humidity in the stratosphere because we believe that the absorption of long-wave radiation by this water vapour plays a very important part in meteorology.

In reply to Mr C. S. Wright: I am rather sceptical about wet-bulb readings higher than the dry-bulb readings. I wonder whether there is any evidence that the thermometers used in Shackleton's expedition had been recalibrated before the paradoxical observations.

Condensation on ice surfaces in the open is a common enough phenomenon, the ice surface being cooled below air temperature. One can sometimes discriminate on a frosty morning between frozen dew and the crystalline ice deposited on the dew. I do not see how this explains the rise of wet-bulb temperature above dry-bulb temperature, both temperatures being taken, presumably, with screened thermometers.

The standard hygrometric tables* in use in Sweden are based on experiments by Ekholm, who attributed high wet-bulb readings to the hygroscopic qualities of muslin. According to these tables the equality of dry- and wet-bulb readings connotes a relative humidity of 97 per cent. I hope that Ekholm's work will be critically examined before the final results of the N.P.L. investigation are published.

One reader of the proof of my paper has raised the question whether the cooling of the water fed to the wet bulb should not be allowed for in the theory. One answer to this question is that the well-ventilated psychrometer in its best known form, that due to Assmann, has not a continuous feed, while in other cases the feed is along a wick which is exposed to the air so that the water is brought very nearly to wet-bulb temperature before reaching the muslin. The more fundamental answer is that even if the water reached the wet bulb at dry-bulb temperature and gave up heat as it spread over the muslin, the allowance for this heat would not seriously affect our analysis. The amendment would be equivalent to a reduction in the value of L, the latent heat, by an amount equal numerically to the difference between the dry- and wet-bulb temperatures. It would not be profitable to attempt to introduce such an amendment.

---

* B. Rolf. *Tables psychrométriques portatives. Calculées selon la formule Svensson-Ekholm* (Stockholm, 1919).

535·214

ON RADIOMETER ACTION AND THE PRESSURE OF RADIATION

By MARY BELL, formerly Lecturer in Physics,

AND

S. E. GREEN, Lecturer in Physics,

Imperial College of Science and Technology

Received July 1, 1932 *and in revised form December* 7, 1932. *Read January* 20, 1933.

ABSTRACT. The experiments here described have arisen from preliminary work conducted with the ultimate object of testing the late Prof. Callendar's formula* for the distribution of energy in the spectrum. The latter experiments, not yet completed, involved radiation-pressure determinations made with a vane suspended in a vacuum sufficiently high for radiometer action to be completely eliminated. While the manner in which radiometer action diminishes as the vacuum improves was being investigated, the series of radiometer effects recorded in the first part of this paper was observed. Radiation was directed upon a light vane suspended by means of a fine quartz fibre in a flask, and the deflections produced when the radiation was incident in turn upon the two sides of the vane were observed for a series of vacuum conditions. The vanes employed included platinized or silvered glass and mica, and also an aluminium vane. The range of air pressure used extended down to about 10^{-6} mm. of mercury.

In the case of the platinized glass vane, at a pressure of a few mm. of mercury the deflections on both the glass and the platinized sides were of the order of those registered at the highest vacua obtained. At pressures of about 10^{-2} mm. gas effects developed which were very large in the case of the glass and mica vanes but much less marked with the aluminium vane. With all the vanes, gas action had practically vanished at a pressure of 10^{-6} mm. of mercury. Under these conditions, measurements of radiation pressure, using glass and mica vanes, were found to give results in agreement with the energy-density of the radiation to within ± 7 per cent.

While the above preliminary experiments were in progress the errors of calculation occurring in Nichols and Hull's paper† on radiation pressure were noticed. Although their work, carried out at a gas pressure of 16 mm. of mercury, has been widely quoted as conclusively establishing, to within about 1 per cent, the numerical equivalence between the pressure and energy-density of radiation, it is found that their results, when correctly evaluated, show a divergence between these quantities of some 10 per cent. Hence Nichols and Hull's investigation cannot be regarded as furnishing a quantitative experimental verification of the equality relationship deducible from theory.

It was therefore thought worth while, using the working experience gained, to attempt more accurate measurements of radiation pressure by the direct method of using metal vanes and a vacuum so high that radiometer action was eliminated. In the second part of the paper the observations and results for all the radiation-pressure measurements are given. With each vane a considerable range of radiation-intensities was employed, the maximum deflections of the suspensions under the influence of the radiation-pressure being up to 10 or 15 times those obtained by Nichols and Hull. The corresponding energy-densities of the radiation were measured by the use of a Callendar cup radio-balance. The

---

* *Phil. Mag.* **27**, 870 (1914).

† *Proc. Amer. Acad.* **38**, 559 (1903).

results for an alloy vane, probably the most reliable of those derived, show that for a number of radiation-intensities the difference between pressure and energy-density varies from + 4 to − 3 per cent. The present experiments are considered in the light of those conducted by other observers. Errors of calculation arising in Nichols and Hull's results are examined in the appendix.

---

§ 1. PRELIMINARY

INTRODUCTION. It is well known that when radiation falls upon a vane suspended in an exhausted vessel the true radiation pressure is obscured, even when the vacuum is of the order of 10^{-4} mm. of mercury, by gas action produced by the heating of the residual air in the neighbourhood of the vane.

This so-called radiometer action has caused difficulty in verifying experimentally the theoretical relationship, originally deduced by Maxwell, between the pressure and the energy-density of the beam, viz. that these two quantities are numerically equal. Of the various attempts which have been made to circumvent gas action, the best known are those of Lebedew* and of Nichols and Hull†. The former made an effort to eliminate it by a suitable construction of the vanes, and the latter by the use of a ballistic method to which reference is made later in this paper. In only two investigations, those of Poynting and Barlow‡ and of Miss Golsen§, has the direct method of obtaining so high a vacuum that gas action becomes negligible been attempted.

Poynting obtained qualitative agreement between pressure and energy-density in the case of absorbing and reflecting surfaces; but, at the highest vacuum used by him, gas action was not entirely eliminated, nor did he investigate the changes in radiometer action at various stages of the vacuum. In 1924, when the work described in the present paper was in progress, Miss Golsen published her results for metal vanes, and showed that with these vanes a vacuum could be obtained at which gas action disappeared. The agreement she deduced between pressure and energy-density of radiation varied from + 6 per cent to − 4 per cent. Nichols and Hull state that their results agree to 1 per cent, but they make errors which are discussed at the end of this paper. Their results for pressure and energy-density, when properly calculated, differ by about 10 per cent.

The work described below was originally undertaken as a preliminary to a more delicate experiment, devised by the late Prof. H. L. Callendar, to test his formula for the distribution of energy in the spectrum of a black body‖. This experiment, which involves the measurement of the radiation pressure produced by different portions of the spectrum, and in which it is most important that radiometer action should be entirely eliminated, has not yet been completed. It has, however, been felt that the preliminary observations may be of interest in view of the fact that the investigation of radiometer action is more complete than that conducted by Miss Golsen; and also because, by a direct method, good agreement between pressure and

* *Ann. d. Physik*, (4), **6**, 433 (1901).

† *Proc. Amer. Acad.* **38**, 559 (1903).

‡ Poynting's *Collected Works*, p. 381; also *Proc. R. S.* A, **83**, 534 (1910).

§ *Ann. d. Physik.* **73**, 624 (1924).

‖ *Phil. Mag.* **27**, 870 (1914).

energy-density values has been obtained over a wide range of radiation-intensities, both with a platinized glass and with a metal suspension.

Oscillation of a vane suspended in a vacuum. In a large number of experiments on radiation pressure, including those described in this paper, the pressure is determined by allowing the radiation to deflect a light delicately suspended vane. Since in the present investigations the damping was so small that the vane was perpetually in oscillation, it is apposite to consider the mode of vibration of such a suspension. The equation of free motion of a vane suspended in a perfect vacuum can, on the assumption that any damping due to the suspending fibre itself is negligible, be written

t

$$\kappa\frac{\partial^2\theta}{\partial t^2}+c\theta=0,$$

κ, c where κ represents the moment of inertia of the suspension and c the torsional
θ constant of the fibre, while θ denotes the angular position at any instant and is given by the solution

A, α

$$\theta=A\cos\left(\sqrt{\frac{c}{\kappa}}\,.\,t-\alpha\right) \qquad \text{......(1).}$$

P, r If radiation falling upon the vane exerts a total force P at an arm r, and the product
L Pr be written L, then the motion satisfies the equation

$$\kappa\frac{\partial^2\theta}{\partial t^2}+c\theta=L,$$

of which the solution is

$$\theta=\frac{L}{c}+B\cos\left(\sqrt{\frac{c}{\kappa}}\,.\,t-\beta\right) \qquad \text{......(2),}$$

B, β the constants B and β being determined by the values of the displacement θ and velocity $\partial\theta/\partial t$ obtaining at the moment of application of the radiation. Denoting
ϕ, v_0 these values by ϕ and v_0 respectively, and taking the instant of application of the light as the new zero of time, we find that

$$B=\{(\phi-L/c)^2+v_0^2\,\kappa/c\}^{\frac{1}{2}}$$

and

$$\beta=\tan^{-1}\frac{v_0\sqrt{(\kappa/c)}}{\phi-L/c}.$$

Relation (2) shows undamped harmonic motion about the mean displaced position L/c, the position at which the couple due to the fibre balances the moment due to radiation pressure. The amplitude B of vibration about this mean position is reduced to zero only when the relations $\phi=L/c$ and $v_0=0$ are together satisfied, i.e. when the amplitude of the initial free vibration of the suspension is L/c, and the radiation is applied when the vane is at the extremity of its swing. The vane then remains steadily displaced in this position.

Thus, with a perfect vacuum, the vibration is perfectly regular about the mean displacement L/c, the turning-points are invariable, and the periodic time is constant. When the light is removed, the vane immediately oscillates about its zero position, with constant turning-points and time of swing, the amplitude of the motion depending on the position and velocity of the vane that obtained when the force was removed.

When the vacuum is imperfect, damping will arise owing to the presence of the residual air. If 2ϵ is the damping-factor, the equation of motion of the vane swinging freely is

$$\kappa \frac{\partial^2 \theta}{\partial t^2} + 2\epsilon \frac{\partial \theta}{\partial t} + c\theta = 0,$$

with the solution

$$\theta = Ce^{-(\epsilon/\kappa)t} \cos (2\pi t/T - \gamma) \qquad \text{......(3);}$$

while when the radiation pressure is applied

$$\kappa \frac{\partial^2 \theta}{\partial t^2} + 2\epsilon \frac{\partial \theta}{\partial t} + c\theta = L,$$

giving the solution

$$\theta = L/c + De^{-(\epsilon/\kappa)t} \cos (2\pi t/T - \delta) \qquad \text{......(4).}$$

Thus in both cases the time of swing T is $2\pi/\sqrt{(c/\kappa - \epsilon^2/\kappa^2)}$, while the amplitude of the oscillations decays exponentially, the logarithmic decrement of the motion being $\epsilon\pi/\sqrt{(c\kappa - \epsilon^2)}$. In practice, however, conditions are more complicated, since damping is not the only effect produced by residual air in the vacuum chamber. Experiments described later showed that, when on application of the light one surface of the vane was raised to a higher temperature than the other, pressures many times greater than the true radiation-pressure were generated. In this case the vane would suffer a mean displacement θ given by $(P \pm R)\, r = c\theta$, where R represents the pressure produced by the heating of the residual air. Such pressures took time to develop and made the time of swing irregular. They also masked the regular decrease of amplitude of motion which would be expected from equation (4). A similar phenomenon was observed on removal of the light from the vane. In this case residual gas effects, which died away slowly, prevented the vane from vibrating about its true zero. These extraneous pressures, usually referred to as radiometer effects, were observed practically to disappear at a vacuum of about 10^{-6} mm. of mercury.

The objects of the experiments here described were firstly to study the variation of radiometer action as the vacuum improved; and secondly to investigate radiation pressure by obtaining so high a vacuum that the only forces acting on the suspensions employed were the true radiation pressure and the restoring elastic forces of the fibre.

As has already been indicated, in such a vacuum the vane will vibrate quite regularly about a mean angular displacement, and the turning-points and period of swing will be quite constant. When the light is removed the suspension will at once oscillate about its zero position, with constant turning-points and time of swing.

On attainment of these conditions it may safely be assumed that the true radiation pressure is being investigated. If, on the other hand, the turning points and time of swing of the vane vary and if, on removal of the light, the vane shows a lag in taking up its oscillation about the true zero, radiometer forces as well as the true radiation pressure are present.

The vanes used in the work to be described were, under experimental conditions, in continual vibration. For brevity, therefore, the term "deflection" is employed to denote the mean position about which the suspension is in oscillation.

§ 2. AN EXPERIMENTAL INVESTIGATION OF RADIOMETER ACTION

The apparatus employed is indicated in plan in figure 1. The optical system *p* was used to project a beam of light from the lamp *l* on to a vane *v* suspended within the flask *f*. This flask, 17 cm. in diameter, was connected through suitable apparatus, shown in figure 2, to the exhausting-system comprising a Gaede mercury-pump outfit.

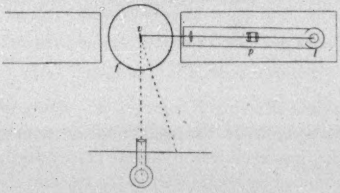


Figure 1. Plan of apparatus.

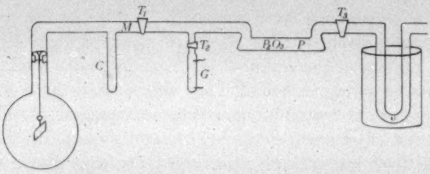


Figure 2. Flask and auxiliary apparatus: *C*, carbon tube; *G*, Geissler tube; *P*, pentoxide tube; T_1, T_2, T_3, taps; *U*, U-tube surrounded by liquid air.

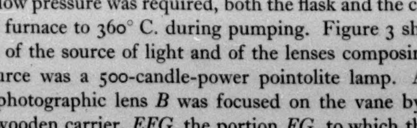


Figure 3. The optical projection system.

When a very low pressure was required, both the flask and the carbon-filled tube were heated in a furnace to 360° C. during pumping. Figure 3 shows in elevation the arrangement of the source of light and of the lenses composing the projection system. The source was a 500-candle-power pointolite lamp. An image of the aperture of the photographic lens *B* was focused on the vane by the achromatic lens *A*. Of the wooden carrier, *EFG*, the portion *FG*, to which the lamp and lens were attached, turned about a pivot P so that an image could be thrown on either end of the vane. As is indicated in figure 1, an appropriate baseboard was fitted on each side of the flask. By transfer of the lamp and projection system from one board to the other the radiation could be made to fall upon either surface of the vane as required.

The vanes were all rectangular in shape as shown in figure 4. In the case of glass vanes the centre piece AB was also of glass, fused to the vane. When a metal vane was used the vane and stem were cut as one piece from the sheet. The vanes were suspended by means of a fine quartz fibre attached at its upper end to a collar which fitted into the neck of the flask. The collar was of gas-free molybdenum supplied by the Vactite Company. The fibre was attached at each end by means of collodion. When this collodion had been gently heated by means of a very small gas flame a deposit of carbon remained which held the fibre well and did not affect the vacuum. Deflections of the vane were read by the lamp-and-scale method, the concave mirror c, figure 4, being used. By means of fine wire this mirror was bound to the stem of the suspension so as to lie at right angles to the vane. Throughout the experiments the scale-distance was of the order of 1 metre.

Details of the suspensions employed are given in table 1.

Table 1

Vane (*a*) Glass, platinized on one side
Vane (*b*) Glass, blackened on one side
Vane (*c*) Aluminium

Vane	Length (cm.)	Mass (gm.)	Moment of inertia (gm.-cm.^{2})	Time of swing (sec.)
(*a*)	3·49	0·340	0·196	52·6
(*b*)	2·25	0·108	0·047	50·5
(*c*)	3·60	0·207	0·047	57·5

The thickness of the glass vanes was of the order of 0·25 mm. The aluminium vane was cut from a piece of foil about 0·05 mm. thick*.

Experiments with the glass vane platinized on one side. (1) To obtain some idea of the degree of vacuum reached in these and subsequent experiments, a McLeod gauge was attached, through a U-tube surrounded by liquid air, to the exhausting apparatus; and at various stages of the pumping the logarithmic decrements of the suspension and the corresponding pressures were noted.

Figure 5 shows the variation of logarithmic decrement with pressure. The values of the logarithmic decrement are given to the base 10. A decrement of 2×10^{-3} corresponded to the lowest pressure read on the gauge, i.e. 4×10^{-4} mm. of mercury.

(2) The McLeod gauge was disconnected from the apparatus and the pumping restarted. At various intervals tap T_1, figure 2, was turned, and the deflections

---

* It is to be emphasized that the effects described in this paper apply only to the case of flat rectangular vanes of the sizes indicated, suspended by means of a quartz fibre, centrally within a glass sphere about 17 cm. in diameter.

produced when a beam of constant intensity was incident in turn upon the glass and the platinized surfaces of the vane were observed. A constant arm was attained by making the edge of the vane a tangent to the circular image. In every case the mean of the deflections for the two ends of the vane was taken. The pressures corresponding to the various deflections were derived from the curve in figure 5. The lowest pressure obtained corresponded to a logarithmic decrement of 6 × 10^{-6} and was thus probably of the order of 10^{-6} mm. of mercury. In this experiment the flask was heated only to about 200° C., while in later work on radiation pressure the flask-temperature was raised to 360° and this, with the further use of a diffusion pump, makes it highly probable that still lower pressures were reached.

Experiments made with the radiation incident upon the platinized surface of the vane showed that all the deflections produced were in the direction of pressure. At a vacuum of 10^{-2} mm. of mercury the deflection was very large, the spot of light which registered the movement of the suspension passing right off the scale. At 10^{-3} mm. of mercury the deflection had noticeably diminished. At a pressure of 10^{-6} mm. the deflection was reduced to about 30 mm. The deflection remained constant at this value during prolonged application of liquid air to the charcoal tube. It was found that the radiation pressure, calculated from this deflection, was in approximate agreement with the energy-density value. Since the logarithmic decrement of the motion of the vane was only 6 × 10^{-6}, damping was obviously negligible. The time of swing of the suspension under the radiation pressure was the same as during free oscillation, and the vibration was perfectly regular about the mean position.

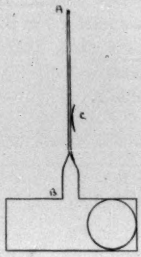


Figure 4.

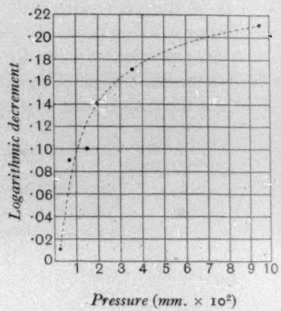


Figure 5. Variation of logarithmic decrement of the suspension with gas pressure.

With the radiation incident upon the glass surface of the vane, the deflections, which were originally in the pressure direction, became increasingly antipressure as the vacuum improved. This antipressure effect was very large when the gas pressure was roughly 10^{-2} mm. At about 2 × 10^{-3} mm., on application of the radiation, a pause occurred before the suction effect began, while at 7×10^{-4} mm. there was a jump in the pressure direction and subsequently a suction effect. With a gas pressure of approximately 10^{-5} mm. of mercury the deflection was found to have changed sign; and it finally acquired a constant positive value (i.e. in the pressure direction) of about 30 mm. at a vacuum in the vicinity of 10^{-6} mm. of mercury. Figure 6 indicates in a general manner, for various gas pressures, the motion of the mean position of the suspension when the radiation was made incident upon the two sides of the vane in turn.

Similar experiments to those described above were conducted with mica vanes. The behaviour already indicated was found to be quite general for all cases in which glass or mica vanes, platinized or silvered on one side, were used.

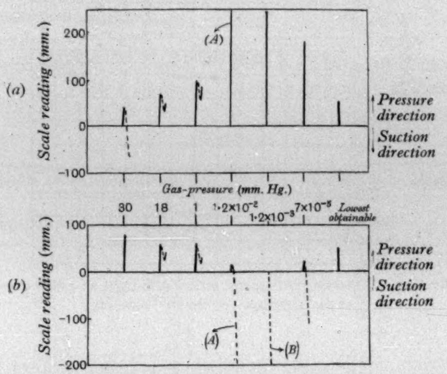


Fig. 6. Variation of deflection of platinized glass vane with gas pressure: (*a*) Radiation on platinized surface; (*b*) Radiation on glass surface*.

Notes. (*A*) Off the scale. (*B*) Off the scale, but with slight arrest before first movement.

Further experiments showing growth and decay of radiometer action at a vacuum of 10^{-4} *mm. Hg, and the disappearance of this action in the neighbourhood of* 10^{-6} *mm.* (1) After pumping to a vacuum of 10^{-4} mm. of mercury, tap T_1, figure 2, was turned, and the beam was allowed to fall on the glass side and kept there continuously. There was a jump of 25 mm. in the pressure direction, then a suction effect showing the growth of radiometer action (see figure 7). This radiometer effect reached a maximum fairly quickly and then decreased very slowly with time—see portion *MP* of the curve. This gradual decay of radiometer action with time when light was continually on the vane and the vacuum was constant occurred whether the radiation was directed on the glass or on the platinized side; that is to say, the deflection apparently tended ultimately to become the true pressure deflection. This rate of decay was so extremely slow at pressures of 10^{-3} to 10^{-5} mm. that the

---

* In this figure deflections in the suction direction are shown by dotted lines. At the pressures of 30, 18 and 1 mm. of mercury, the actual movements of the vane, before coming to rest, are given. The high degree of damping at these pressures is thus illustrated. At the lower pressures only the final mean position of the vane is indicated. The damping decreased rapidly after about 10^{-1} mm. and was negligible at 10^{-6} mm.

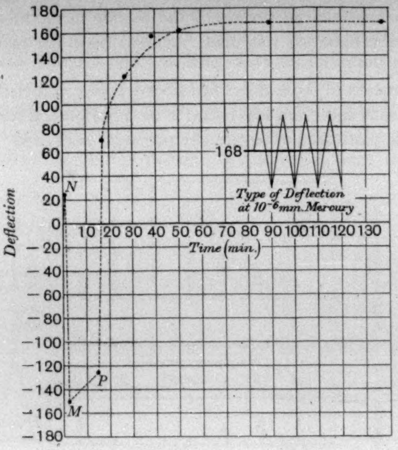


Figure 7. Illustrating radiometer action with light on glass surface, at gas pressures 10^{-4} to 10^{-6} mm. Hg.

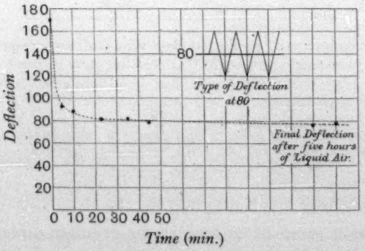


Figure 8. Illustrating radiometer action with light on platinized side at gas pressures from 10^{-4} to 10^{-6} mm.

possible complete disappearance of radiometer action, which might be inferred, was never actually observed. As will be seen later, the effect at higher vacua was much accelerated.

Without the light being removed from the vane the vacuum was now brought down to about 10^{-6} mm. by applying liquid air to the carbon-filled tube. Following the change of vacuum the deflection quickly became a pressure effect, and the vane eventually oscillated regularly about a fixed mean position during prolonged application of liquid air. This is shown in the inset figure, where the new time scale is such that the distance between successive maxima is the period of the suspension (about 53 sec.). Although denoted by straight lines for convenience, the oscillations were in fact simple harmonic, and the vibration is of the exact type given by equation 2, page 322.

(2) A similar experiment was carried out with radiation incident upon the platinized side of the vane (see figure 8). In this case an initial deflection of 170 mm., produced by applying the radiation at a vacuum of 10^{-4} mm., was reduced in 25 minutes to a steady deflection of 80 mm. on the application of liquid air to the carbon-filled tube. The turning-points at this highest vacuum were regular during prolonged application of liquid air, as shown in inset figure 8, where all considerations mentioned above regarding inset figure 7 again apply.

Radiation was next directed upon the glass and platinized sides respectively at a vacuum of 10^{-6} mm. Table 2 shows the observed deflections in millimetres of scale.

Table 2

Radiation on platinized side			Radiation on glass side		
Turning-points		Deflection from zero	Turning-points		Deflection from zero
L.	R.		L.	R.	
54	203	75	228	87	70·5
57	195	69	236	83·5	76
56	195	69·5	237	82·5	77
56	193·5	68·5	238	82·5	77·5
56·5	193·5	68·5			

A study of the deflections shows that even at this high vacuum radiometer action existed initially to some extent. The quick growth (see page 327, line 18) is not here apparent, as it is masked by the relatively long period of the suspension, but the presence and the decay of radiometer action can be detected. On the platinized side the deflections diminish until they reach a steady value, i.e. on the platinized side the gas action exists initially as a pressure and gradually disappears. On the glass side the deflections rise until they reach a steady value, i.e. the radiometer action is an anti-pressure effect and gradually disappears. Ultimately the deflections have constant turning-points, the time of swing is constant, and the logarithmic decrement is negligible, i.e. in every way the oscillations conform to equation (2).

It may be objected that even in these circumstances the entire absence of radiometer action is not proved. Some constant gas action might conceivably be present in conjunction with the true radiation pressure. From radiation-pressure experiments with an aluminium vane, strong additional evidence was, however, forthcoming that when the vibrations of this aluminium vane conformed exactly to equation (2), radiometer action was entirely absent. It seems therefore reasonable to assume that if the same equation is satisfied in the case of the glass suspension, gas action has been completely eliminated.

One further effect was observed. The final deflections on the platinized and glass sides were not equal, but the former were always less than the latter as illustrated in table 3. Incidentally this table also illustrates for various radiation-intensities the decay of radiometer action just described.

The difference between the final deflections on the two sides is thus of the order of 16 per cent. The data given in the table were obtained during experiments upon the pressure of radiation described later*. The mean reflecting power (see table 8) on the platinized side of the vane was 67 per cent and upon the glass side 65 per cent. It is therefore impossible to explain the recorded divergence between the final deflections on the basis of a divergence in the reflecting power on the two sides. Again, radiometer action, as has been shown, always tends to increase the deflection on the platinized side and to decrease that on the glass side. The divergence between the final deflections cannot, then, be put down to residual radiometer action unless, as seems very improbable, this changes sign at very low pressure. Incidentally there seems to be here further support for the view that radiometer action has vanished at these very low pressures.

Table 3

Beam	Platinized side		Glass side	
	Deflections		Deflections	
	First	Final	First	Final
1	48·0	37·6	34·1	44·2
2	78·1	65·4	72·9	77·2
3	96·1	88·2	93·2	102·7
4	118·0	112·6	123·2	126·6
5	132·0	116·7	132·2	140·2
6	155·5	150·6	160·2	170·6

The suggestion is put forward that the effect may be due to the fact that the radiation absorbed by the film (some 35 per cent of the incident radiation) is reradiated on one side through glass and on the other through a vacuum.

Assuming that this absorbed energy is reradiated on the glass and vacuum sides in the ratio of $\mu^2 : 1$, taking a tentative value of μ as 1·5, and assuming also that this reradiated energy is not absorbed by the glass, we find that the correction for the reaction on the vane due to reradiation reduces the disparity between the deflections from some 16 per cent to about 5 per cent, while leaving the final mean value unaltered.

Figure 9 shows in a very general manner, and not to scale, the deflections of the suspension when the radiation was kept permanently on the vane as pumping continued. It will be noticed that at a pressure of a few millimetres of mercury the deflections for both the glass and the platinized surfaces are approximately equal to the true radiation deflection. These curves were taken for three different radiation-intensities and are of interest in that they appear to corroborate Nichols and Hull's observation that, with a gas pressure in the vicinity of a few millimetres of mercury, the resultant of combined gas actions has so small a value that the deflection of the vane is of the same order as the true radiation deflection. Owing to the rapid change of vacuum obtaining in these experiments, it must be emphasized that no deductions other than that just mentioned can be made with regard to gas action.

---

* A second platinized glass vane was used for these later experiments. Data relating to this suspension are given, in connection with the radiation pressure work, on p. 338.

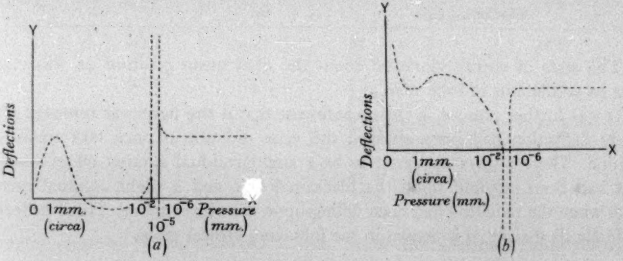


Figure 9. (*a*) Platinized surface. (*b*) Glass surface. Variation of deflections with the light continuously on the vane as pumping continued.

Summary. The experiments already described are typical of a large number conducted with silvered and platinized glass vanes. In every case the following general results were established:

(*a*) At a pressure of a few millimetres of mercury the deflections on both the glass and the platinized sides were of the order of those registered at the highest vacuum obtained. (*b*) At pressures of about 10^{-2} mm. large gas effects developed and were apparent as a suction on the glass side and as a pressure on the platinized side. If D_P denote the deflection due to radiation pressure, D_R the deflection due to gas action and D the resultant deflection, then $D_R + D_P = D$ where D_R is negative for the glass surface and positive for the platinized surface. (*c*) D_R took time to develop, reached a maximum and then tended to die away very slowly. (*d*) The higher the vacuum the less was the gas action, and D_R eventually became less than D_P. When this occurred D was positive on both surfaces. (*e*) At a vacuum of the order of 10^{-6} mm., when D_R was very small no initial growth of gas action was apparent, but the much slower decay was easily observed. The mean value of the final steady deflections was now taken to give the true radiation pressure. (*f*) The final steady deflection on the glass side was always greater than that on the platinized side.

D_P, D_R
D

Experiments with the glass vane blackened on one side. In the case of this vane the flask was heated to 360° C. during pumping, and the carbon tube was immersed in liquid air for a long time prior to the application of the radiation. Even with these precautions there was a large amount of residual gas action, shown by the fact that the initial deflection on the glass side was very much smaller than that on the blackened side, and the deflections only became equal after an appreciable time interval. Typical data are as follows:

Table 4. (Light continuously on the vane)

	Initial deflections	Final deflections
Glass side	27	42
Blackened side	64	42

The state of steady vibration about the final mean position 42 was reached after 10 oscillations in each case.

It was further noticed in this experiment that if the light was removed after a steady deflection had been attained the vane did not at once take up its zero position. There always appeared to be a slight residual suction effect when the light had been incident upon the blackened side and a slight residual pressure effect when the radiation had been falling upon the glass surface. These deflections gradually died away as is shown in the following typical table.

Table 5

	Steady-pressure deflection	Residual deflections after removals of light
Glass surface	35	(Pressure) 5·5, 2·5, 1·5, 1·0
Blackened surface	42	(Suction) 9·0, 5·5, 3·5

The above table shows that with residual radiometer action the vane does not at once take up the original zero when the radiation is removed.

The time interval separating the consecutive deflections given in the third column was about 51 sec., the period of the suspension. It may be said that, with this vane, gas action was in every way similar to, but very much larger than, that with the platinized vane.

Experiments with the aluminium vane. When the vacuum was of the order of 10^{-6} mm. the vane assumed its final condition of steady vibration directly the beam of light was allowed to fall upon it (compare the residual gas effects with glass vanes already mentioned) and fell to vibration about its original zero immediately the light was removed.

In Table 6 are given deflectional observations in millimetres of scale with beams of different intensities with a vacuum of about 10^{-6} mm. pressure.

These observations illustrate the steadiness of the zero and also of the turning-points.

When the vacuum was inferior the deflection of the vane did not at once assume its final value, and the zero wandered.

Table 6

Beam	Zeros		Turning-points with beam on vane			Deflection
	Before deflection	After deflection				
	Left	Left	Left		Right	To the right
I	43·5	44	79·5	0	58·5	33·2
			79·5		58·5	
II	43·7	43·7	85	0	80	40·8
			86·5		80	
III	43·7	43·7	70	0	81·5	49·4
			69·6		81	
IV	43·7	43·4	77·5	0	110	59·9
			77·4		110	
V	43·4	43·4	17·5	0	42·8	73·7
			17·5		43·4	
			17·5		43·2	

General remarks on the observed effects. Since the platinum film reflected 65 per cent only of the incident light while producing practically no scattering, it absorbed 35 per cent of the radiation falling upon it. The glass plate was found experimentally to absorb about 4 per cent of the incident light. The mass of the platinum film was roughly one-fifth of that of the glass plate. The specific heat of the film (assuming this constant to be the same for the sputtered material as for the substance in bulk) was 0·03, that of the glass 0·2. Hence the thermal capacity of the platinum film was much less than that of the glass plate. It follows that the film always rose to a higher temperature than the glass plate, whether the light fell upon the glass or upon the platinized surface of the vane. Calculation showed that the temperature-difference between the surfaces was of the order of 0·1° C. In accordance with the usual explanation* the velocity of recoil of the molecules meeting the hotter surface must be greater than the velocity of approach. This gives rise to a pressure on the heated surface, and strictly speaking this pressure only is referred to as "radiometer action." Thus, radiometer action will always be a pressure on the platinized surface of the vane, whether the radiation is incident upon the platinized surface or upon the glass surface. Consequently the radiometer effect will be in the same direction as the radiation pressure when the light is incident upon the platinum film, and in the opposite direction when it falls on the glass side; i.e. there will apparently be a pressure effect in the former case and a suction effect in the latter.

At the higher gas pressures it is probable that convection is an important factor. Reference to figure 6 shows that the total gas action reaches a maximum at pressures of 10^{-2} to 10^{-3} mm., and from the directions of the deflections it looks as though

* Poynting, *Heat*, pp. 150, 151 (1922).

radiometer action had now become the only gas effect. The very large value at these pressures may possibly be connected with the fact that the mean free path of the residual gas molecules is now of the same order as the dimensions of the vane. Obviously radiometer action must become negligible at a sufficiently high vacuum.

In his discussion of radiometer action, Poynting* states that over the surface of the vane the extra pressure produced by the heated molecules would be quickly compensated by an adjustment of density of the gas, but that the compensation is not complete at the edge of the vane, so that persistent radiometer action is really an edge effect. Experiment showed that at pressures of 10^{-2} to 10^{-4} mm. radiometer action died away extremely slowly, though it decayed quickly at lower pressures, possibly owing to the greater mobility of the gas. All the experiments recorded, however, were performed with vanes not materially differing in size or shape and with air or oxygen as the residual gas. Thus the results given apply only to these particular conditions and throw no light on the existence of a possible edge effect, or on the influence of the nature of the residual gas. If it were possible to assume that the density compensation at the surface of the vane mentioned by Poynting proceeded very slowly at 10^{-2} to 10^{-4} mm. and more quickly at 10^{-6} mm., the gradual fall in deflections on the platinized side and the gradual rise on the glass side until the steady state was attained, and also the lag in returning to the true zero, when the radiation was removed, could be explained without reference to an edge effect. In any case it is probable that the lag effects observed are connected with the time taken for the entire system to acquire the thermal steady state.

There was found to be an absence of regular gas effects with the aluminium vane. Such effects as were present were very small, had a maximum value at about 10^{-3} mm., and had entirely ceased at a pressure of 10^{-6} mm. This was to be anticipated in view of the high thermal conductivity and thinness of the vane. The two surfaces of the latter would be at practically the same temperature, so that no perceptible gas action could arise. Miss Golsen also found maximum radiometer effects at a pressure of about 10^{-2} mm. and states that at a pressure of 10^{-6} mm. radiometer action ceased with a metal vane.

All the vanes were heated to 300° C. in a vacuum before being mounted in the flask. For this reason, and also because the radiometer effects were extremely regular, it is unlikely that they can have been in any way due to escape of gas from the surfaces of the vanes during the experiments. All the results mentioned were perfectly definite and reproducible.

§ 3. DETERMINATION OF THE PRESSURE OF RADIATION AND THE COMPARISON OF THIS PRESSURE WITH THE ENERGY-DENSITY

Apparatus and general procedure. For these measurements the apparatus employed consisted of the following: (1) a light vane of glass or metal suspended in an exhausted flask; (2) an optical system comprising a gas-filled Osram lamp and suitable lenses so arranged that the radiation from the lamp could be directed upon either of the surfaces of the vane; and (3) a Callendar cup radio-balance* to measure the intensity of the beam and the reflection coefficient of the vane.

---

* Poynting, *Heat*, 150, 151 (1922).

The arrangement of the apparatus and the procedure followed in the evacuation of the system were the same as in the investigation of radiometer action (see figures 1, 2 and 3) with the two exceptions that the Gaede mercury pump was eventually replaced by a mercury diffusion pump backed by the Gaede pump, and that, with the object of improving the vacuum, the carbon tube and flask were heated to higher temperatures during evacuation. A good vacuum was obtained when flask and tube were heated to 360° C. for eight hours or more during pumping; the temperature of flask and carbon tube were then slowly reduced to normal while pumping continued. Taps T_1, T_2 and T_3, figure 2, were then closed in order, and the furnace was removed. An asbestos case was placed round the flask, and when the vane had lost the extraneous motions produced by these operations the carbon tube was surrounded by liquid air and observations were taken. In the earlier experiments the flask was sealed off from the exhausting apparatus by means of an electric furnace surrounding the arm *M*, figure 2. This operation appeared, however, to be unsatisfactory, for two reasons. In the first place gas was emitted from the red-hot glass and thus the vacuum was impaired, and secondly great risk was involved of spoiling the experiment by some accident. Specially prepared tap grease was used for T_1, figure 2. From the excellence of the vacua obtained after the carbon tube had been surrounded by liquid air, it was obvious that the vapour pressure of the grease had a negligible effect. A further great advantage of this arrangement was that a series of evacuations could be performed without disturbing the flask and the suspended system within it. The vanes used were heated to 360° C. in a vacuum before being mounted in the flask.

In adjusting the position of the suspension within the flask two conditions had to be satisfied. The vane had to lie at right angles to the direction of the beam, and at an elevation within the flask such that no radiation was reflected back from the flask surface to the vane. The image produced by the flask of the focused spot on the vane was readily seen within the flask, and the vane was so adjusted that this image fell just below it. After the necessary adjustments had been carried out by means of the collar in the neck of the flask the latter was sealed to the exhausting apparatus.

For some experiments the quartz fibres employed were made by the bow-and-arrow method; but the more delicate ones were drawn out by means of an oxy-hydrogen blowpipe by a method shown to the authors by Dr W. F. G. Swann. These very delicate fibres showed colour in sunlight. The finest ones, of a blue colour, were not strong enough to support the suspension. Those exhibiting a red colour were used. The fibres were attached to suspension and collar by a fine carbon layer by the method already described.

The 1000-watt filament lamp used as the source of light was connected to a steady 110-volt supply, the potential-drop across the lamp being maintained constant by means of a resistance in circuit. The lamp was found to remain very steady over long periods.

---

* *Proc. Phys. Soc.* **23**, 15 (1910).

Calculation of the radiation pressure. The following system of symbols is employed:

m — m is the reflecting power of the vane;
P — P the required pressure of the radiation;
A — A the area of the spot of light on the vane;
r — r the arm at which the radiation pressure acts;
c — c the fibre constant, i.e. the couple necessary to turn the suspension through unit angle;
θ — θ the mean angular deflection of the vane;
T — T the periodic time of the suspended system; and
I — I the moment of inertia of the suspension (vane and concave mirror).

The pressure of the beam was deduced from the relations

$$(1+m)\,PAr = c\theta \quad\text{and}\quad T = 2\pi\sqrt{\frac{I}{c}} \qquad \text{......(5) and (6),}$$

which give

$$P = \frac{c\theta}{(1+m)\,rA} = \frac{4\pi^2 I d}{T^2 rA\,(1+m)\,2D} \qquad \text{......(7) and (8),}$$

d, D — where d and D denote respectively the scale deflection and the distance between the scale and the mirror on the stem of the suspension. Correction of the value of $d/2D$ to give the true angular displacement of the suspension was in most cases too small to justify application. For the same reason, correction for the fact that, in the displaced orientations of the vanes, the radiation was not quite normally incident could in general be disregarded.

The lens system was so arranged that the ends and two edges of the vane could be made tangents (see figure 4) to the focused image of the aperture of lens *B*, figure 3. Thus from the known dimensions of the vane the area of the image (*A* above) and the arm *r* at which the light-pressure acts could be calculated from the relations

$$A = \pi\left(\tfrac{1}{2}b\right)^2 \quad\text{and}\quad r = \tfrac{1}{2}(l-b) \qquad \text{......(9) and (10),}$$

where l and b denote respectively the length and depth of the vane.

In some cases the area of the spot was deduced from the aperture of the photographic lens *B*, figure 3, and the appropriate constants of the optical system. The deflection d was determined for each end of the vane as well as for both surfaces.

Determination of the reflecting power of the vane. The measurement of the reflection coefficient of the vane was performed in a subsidiary experiment, the incident and reflected intensities being observed by means of the radio-balance*. The optical arrangement employed for the production of direct and reflected beams was similar to that adopted by Nichols and Hull, and is shown diagrammatically in figure 10. In this diagram *M* is a concave mirror, *RB* the radio-balance and

---

* The method of deriving the radiation-intensities is indicated on p. 338.

V the vane fixed in an upright at the centre of the turntable *T*. The full line indicates the path of the radiation when directly incident upon the concave mirror and radio-balance, and the dotted line the direction of the beam when reflection takes place at the surface of the vane.

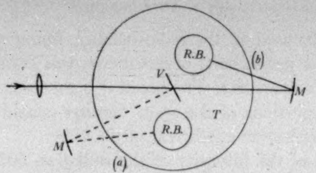


Figure 10. Indicating the method of measuring the reflecting powers of the vanes.

The procedure was first of all to cast a sharply focused spot of light on to the vane by means of the projection system used in the deflectional observations. An image of this spot of light was cast on to the radio-balance by placing the concave mirror and balance in position *a*, figure 10. In this position reflected radiation-intensities were measured. The incident intensities were determined after removal of the vane and rotation of the turntable into position *b*. The diameter of the spot of light used was varied, as required, by the use of a series of different apertures for the photographic lens *B*, figure 3. In preliminary experiments on reflecting power a number of types of thermopile were tried. Owing to the large uncertainties in the results arising from parasitic effects in the thermocouple circuits, it was necessary eventually to abandon the thermopile as the measuring instrument in favour of the radio-balance, which gave unambiguous and reproducible readings.

Since the vane was used in a vacuum, while the reflecting power was measured in the air of the laboratory, the assumption is involved that the reflection coefficient would not be substantially different in the two cases.

Measurement of the energy-density of the radiation. In determining the energy-density of the beam, previous investigators have had recourse to the indirect method of measuring the heat absorbed when the radiation was incident upon a given mass of a substance of known specific heat. Over such methods, which involved long experiments and complicated apparatus, the use of a Callendar radio-balance carried the great advantage that measurements could thereby be rapidly made to give the intensity of the radiation directly in watts per square centimetre. The latter was deduced from the relation

$$aH = 2PC + (D - D')/s \qquad \text{......(11)},$$

in which a is the area of the balance cups, H the intensity of the beam, P the Peltier coefficient of the thermocouple junctions at the temperature indicated by a thermometer mounted in the instrument, C the neutralizing current and s the sensitivity of the galvanometer. D and D' denote the small deflections of the galvanometer obtaining when the radiation falls into the balance cups in turn.

a, H, P

C, s

D, D'

The term containing these deflections in the above expression constitutes a small correction.

If aH be the value in watts of the energy received per second by the balance, the energy-density of the radiation is

$$\tfrac{1}{3}H \times 10^{-3}\ \text{erg/cm.}^3$$

The spot of light focused on the radio-balance, being of the same size as that on the vane during the deflectional observations, was considerably larger in diameter than the balance apertures. The mean was therefore taken of a number of readings for different portions of the spot. Similar considerations applied to the determinations of the reflection coefficient of the vane.

For the evaluation of the intensity of the radiation falling upon the vane the radio-balance results required correction to allow for the energy loss due to the flask. The determination of this correction is considered later.

Measurements with a platinized glass vane. A series of determinations were made with a glass vane platinized on one side. The vane was exactly similar to that used in the later parts of the investigation of radiometer action (see page 329).

Specimen data and calculations involved in one typical determination of the radiation pressure with this vane are as shown in tables 7 and 8, and below.

When measuring the reflecting power of the vane, a large number of readings were taken, as the results varied to a considerable extent and the reflection coefficient constituted a large correction in evaluating the radiation pressure. A rather small spot of light was used in these determinations. The data given below show that the reflecting power was fairly constant over the right-hand side of the platinized surface and both sides of the glass surface, but varied over the remaining part of the platinized surface. Some of the figures given in table 8 were mean values taken from several readings.

Table 7. Deflections (mm.) of vane under the influence of the radiation
(Scale distance $D = 110{\cdot}7$ cm.)

Beam incident upon	Left-hand-side turning-points			Deflection from zero	Right-hand-side turning-points			Deflection from zero
	Left		Right		Left		Right	
Platinized surface	181·5	o	18	81·7	54	o	203	74·5
	154		24·5	64·7	57		195	69·0
	150		26·5	61·7	56·5		195	69·5
	151·5		25·5	63·0	56·5		193·5	68·5
	151·5		27	62·2	56·5		193·5	68·5
	151·5		27	62·2				
Glass surface	228·5	o	87	70·7	18	o	168·5	75·2
	236·5		83·5	76·5	18·5		169·5	75·5
	237·5		82·5	77·5	17·5		170·5	76·5
	238·5		82·5	78·0	17·5		169	75·7
	237·5		81·5	78·0	16·5		170·5	77·0
	238		82	78·0				
				Mean deflection on platinized side				65·4
				Mean deflection on glass side				77·2
				Final mean				71·3

Table 8. Reflecting power (per cent)

Platinized surface		Glass surface	
Left-hand side	Right-hand side	Left-hand side	Right-hand side
68·0	72·6	64·2	63·8
62·2	71·4	64·2	67·7
57·5	70·6	63·2	66·6
58·0	70·0	62·1	65·6
63·7	69·6	65·4	67·3
67·5	69·0		
64·3	70·8		
62·2	71·4		
—	73·1		
Mean values: 62·9	70·7	63·8	66·2
Final mean value of reflecting power 65·9			

Calculation of the light-pressure:

Area of the spot, $\pi\left(\frac{1{\cdot}3087}{2}\right)^2$ cm^2.

Period of the suspension, 67·2 sec.
Deflection, 71·3 mm.
Arm, 0·933 cm.
Moment of inertia of suspension, 0·1485 cm^2.
Scale distance, 1107 mm.
Reflecting power of vane, 65·9 per cent.

Hence from relation (8) on p. 336,

$$P = 20{\cdot}1 \times 10^{-6}\ \mathrm{dyne/cm^2}.$$

Measurement of the energy-density of the beam. After each deflectional observation the optical system was turned so as to direct the radiation upon the radio-balance, and a series of energy-determinations were carried out. On the completion of these sets of experiments the reflection coefficient of the vane and the energy-loss due to the glass of the flask were measured. The latter was found by allowing the radiation to fall upon the radio-balance (*a*) directly and (*b*) through the flask. A number of readings for the energy received by the balance were taken, and it was found that the mean value of the loss due to the two sides of the flask was 21·8 per cent, giving for one side 11·6 per cent*.

The mean value of the energy falling per second upon the radio-balance apertures of area *a* when the radiation was directly incident was 2213 μW. Reducing this by 11·6 per cent we have 1956 μW. as the value of the energy falling on the vane per second per 0·03467 cm.^{2} Thus the energy-density of the beam exerting a pressure of 20·1 × 10^{-6} dyne/cm.^{2}, i.e.

---

* Tests conducted with the flask (*a*) exhausted to about 0·1 mm. and (*b*) containing air at atmospheric pressure gave no systematic divergence in results. Thus any effect due to the presence of air between the flask surfaces must, if existent at all, have been small. This justified the later adoption of the more direct method of determining the energy density subsequently described.

$$18{\cdot}8 \times 10^{-6}\ \text{erg./cm.}^3$$

Since the flask was large and the light entered practically normally at the equator, no appreciable distortion effect due to the transmission through the flask could be observed. In later experiments any possible distortion was automatically corrected by taking all the energy-determinations after the pressure-deflections. The piece of glass through which the light had passed was cut from the flask and placed in front of the radio-balance at exactly the same distance as it had been from the vane. Thus the optical conditions obtaining during the energy-determinations reproduced exactly those of the deflectional observations. All subsequent determinations by this more accurate method with flasks similar to the one referred to above gave an energy-loss due to the flask of about 9 per cent. It therefore seems reasonable to suppose that the result, 11·6 per cent, was about 3 per cent too high. This may in part account for the fact that in this experiment (see figure 11) the energy-density was always less than the pressure.

Further determinations with the platinized glass vane. A series of similar measurements were made with this suspension. Various values of light-pressure and corresponding energy-density of beam were obtained by placing the lamp in different positions relative to the rest of the optical system. The mean values of the deflections on the platinized and glass surfaces are given in table 9.

Table 9. Deflections (mm.) of the vane under the influence of the radiation

Beam	Platinized surface	Glass surface	Mean
1	37·6	44·2	40·9
2	65·4	77·2	71·3
3	88·2	102·7	95·5
4	112·6	126·6	119·6
5	150·6	170·6	160·6

Corresponding energy determinations are as follows:

Table 10. Radiation-intensities (W. × 10^{-5} per 0·03467* cm.^{2}) with beam directly incident upon balance

Beam	1	2	3	4	5
Intensity	124	231	309	363	501
	121	221	305	374	515
	126	207	295	365	487
	133	221	299	368	496
	—	226	312	376	501
Mean	126	221	304	369	500
Less 11·6 %	111	195	269	326	442

* Aperture of radio-balance cups.

The value (11·6 per cent) of the correction for the loss due to the flask which is mentioned both in the above table and in the earlier specimen calculation was the mean figure deduced from experiments with a variety of radiation-intensities.

Experiments with a mica vane. A set of similar experiments were conducted with a mica vane platinized on one side.

The final results deduced with the glass and mica vanes are plotted in figure 11.

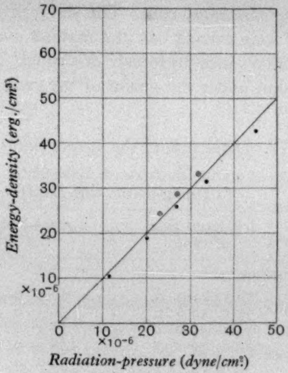


Figure 11. Results obtained using glass and mica vanes.
⊙ Mica vane • Glass vane

Later determinations with metal vanes. For various reasons the results given above for the platinized vanes were not considered to show the highest degree of accuracy obtainable by this direct method. They did however demonstrate that radiation pressure could be measured by it, and that therefore the experiment devised by Prof. Callendar could be proceeded with. This had been originally the fundamental issue. In the meantime, however, the errors occurring in Nichols and Hull's calculations had been noticed; it therefore seemed worth while to use the experience already gained to attempt more accurate measurements of pressure and energy values.

In this new experiment the material of the vane was aluminium. This metal was selected for its lightness and high thermal conductivity, and for the fact that it was already known that with a vane of this material radiometer action had entirely disappeared at a vacuum of 10^{-6} mm. of mercury. Various further points had to be considered. Since the pressure to be measured was extremely small, it was essential that a delicate fibre be used. Again, an important point was to find a workable value for the period of the suspension. If the period is too long, not only do the observations become tedious but the source of light may vary during the experiment. It was found that the end points could be accurately read and other conditions satisfied when the period was about one minute. The sensitivity of the suspension could not profitably be raised by increasing the length of the vane, and with it the arm *r*, since to do so would unduly increase the moment of inertia and hence the time of swing. The experimental setting of the spot into the correct position might appear to be one of the most doubtful features of the work, but an examination of tables 11 and 13, which give readings by different observers, will show that this setting can be made with an accuracy not inferior to that obtained in other parts of the experiment.

Determinations with an aluminium vane. The series of observations conducted with an aluminium vane were carried out in a manner similar to that adopted in the cases of the non-metallic vanes previously described. Typical readings for the deflection of the suspension under the action of the radiation pressure are given in table 11.

Table 11. Deflection of the suspension (mm.)

Zero positions		*Turning-points with radiation on		Deflection
Before deflection	After deflection	left-hand side of vane	right-hand side of vane	
Radiation-intensity 1				
6·0	7·2	76·5 41·5 0	37·0 0 195·0	68·9
		75·5 40·0 0	36·5 0 197·5	
		75·4 39·8 0	37·5 0 197·5	
7·2	7·0	80·0 39·0 0	38·5 0 197·5	69·1
		78·5 38·0 0	38·0 0 198·0	
		78·0 38·0 0	38·0 0 198·0	
		78·8 38·5 0		
7·0	7·5	69·0 50·0 0	46·0 0 203·0	67·0
		68·0 49·0	46·0 202·0	
		67·8 48·5 0	46·0 202·0	
7·5	7·5	78·0 40·5 0	0 60·0 96·5	68·8
		78·0 41·0	60·0 97·0	
7·0	—	83·5 35·5 0	0 50·0 103·4	68·1
			0 50·0 103·4	
Radiation-intensity 2				
6·5	—	106·0 37·5 0	0 63·5 112·5	78·8
		105·5 37·5	64·0 113·0	
		208·0 0 67·0	0 46·0 132·0	80·0
		208·5 67·0	46·0 132·3	
		130·5 12·0 0	0 70·0 106·5	79·7
		130·5 11·6 0	70·0 107·0	
7·2	6·7	133·0 11·5 0	0 67·0 110·0	80·2
		132·0 11·5	67·0 110·0	

For the above and other intensities of radiation employed, the steadiness of the zeros of the suspension and the constancy of the amplitude of swing showed that gas action had been eliminated.

---

* It is to be remembered, that, with a fixed incident beam, while the mean deflection is constant, the amplitude of swing about this mean position varies with the velocity and position of the vane obtaining when the light was applied (see page 322). The amplitude, when once assumed, will then remain invariable.

With this vane two experiments were performed by evacuating the system twice, all conditions with the exception of the distance of the scale from the mirror being exactly reproduced.

A summary of the deflections and the energy-density values is given in table 12.

Table 12

Energy-density (erg/cm³)	Deflection of vane (mm.)
Evacuation 1. Scale distance 102 cm.	
$12{\cdot}2 \times 10^{-6}$	68·4
14·5	79·6
21·6	116·2
30·1	166·3
Evacuation 2. Scale distance 123 cm.	
$10{\cdot}8 \times 10^{-6}$	72·0
15·4	102·1
24·0	160·7
36·2	243·8

Unfortunately the surface of the aluminium changed during the determinations of the deflections of the vane, owing perhaps to the high temperature to which the metal was subjected or to the presence of a trace of mercury during the evacuation. Light on leaving the vane was found to be so scattered that the reflection coefficient could not be measured accurately. As nearly as could be estimated the value came to 42 per cent. With this value it was found that the calculated values for pressure and energy-density of radiation differed consistently by about 12 per cent. The pressures plotted against the energy values are given in figure 12. It will be seen that the results for the two evacuations lie closely on the same straight line, which on production passes through the origin. The fact that the ratio of calculated pressure to energy-density of radiation, while differing appreciably from unity, was thus constant both for varying intensities of radiation and for two independent evacuations, may be regarded as affording conclusive evidence of the absence of radiometer action. This is further supported by the regularity of the turning-points and zeros of the suspension illustrated in table 11*. It may be remarked here that with the platinized glass surface there was practically no scattering, so that as far as optical properties were concerned it was found to be greatly superior to all metal vanes—with the possible exception of the alloy vane used later.

Determinations with an alloy vane. Since the surface of the aluminium vane was found to be unsatisfactory, tests were made as to the suitability of other metals for the vane material. The metal finally adopted was an alloy consisting largely of copper and nickel. Tests using high magnetic field-strengths showed that the magnetic properties of this material were no more pronounced than those of such substances as glass and copper. Further, after the erection of the apparatus had been completed the periodic time of the suspension was found to be unaffected by a strong magnetic field. It was therefore justifiable to assume that the deflections of the vane would be unaffected by a slight variation in the magnetic field of the laboratory, if such occurred.

---

* Thus while it was not possible to deduce the absolute value of the pressure of radiation, the observations taken with the aluminium vane were of great interest for two reasons. They showed conclusively that radiation pressure is proportional to the energy-density, and also that radiometer action can be completely eliminated with a metal vane.

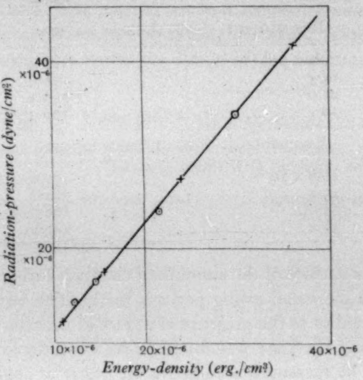


Figure. 12. Results obtained with aluminium vane.

Observations (1)*: evaluation of radiation pressure.* Data relating to the suspension:

Linear dimensions of the vane: length 21·93 mm., depth 11·02 mm.
Moment of inertia of suspension, 0·0903 gm.-cm.^{2}
Periodic time of suspension, 67·6 sec.
Scale distance, 104·3 cm.

Determinations were made of the deflections produced with the radiation incident upon all four end faces of the vane in turn. In this experiment there was found to be a slight regular drift of zero having a period of about 40 minutes. This was very persistent, lasting over several days, and probably arose from pendulum motions of the suspension. By taking the deflectional readings during the intervals of maximum displacement of the zero, i.e. when the rate of change of zero was a minimum, the effect of the periodic wandering was practically eliminated.

In the case of the majority of the observations given in table 13 the beam was quickly turned from one end of the vane to the other without an intermediate checking of the zero. The double deflection was thus directly observed.

Table 13. Deflectional data (mm.)

Beam	Deflections when beam was directed on		Final mean
	left-hand surface of vane	right-hand surface of vane	
1	44·2	46·9	
	45·5	45·7	
	44·8	45·6	
	44·3	45·7	
	44·6	—	
	44·1	—	
Mean	44·4	46·0	45·2
2	64·7	64·8	
	64·6	66·0	
	65·1	63·4	
	62·4	65·0	
	64·8	66·7	
	66·2	65·8	
Mean	64·6	65·3	65·0
3	84·4	91·0	
	85·6	85·6	
	82·7	—	
Mean	84·2	88·4	86·3

There is a rather large discrepancy in the results for the last series. This is probably due to the fact that with a beam of such a high intensity the accurate setting of the spot presented some difficulty.

Reflecting power of the vane. Two of the reasons for using this material were that it took a high polish and that it possessed considerable rigidity in thin layers, so that when once flattened the vane surfaces were not easily impaired. Moreover the material reflected light regularly with very little scattering, and was unaffected by the preliminary heating of the flask. Determinations of the reflection coefficient of the vane, made after the main experiment by means of the radio-balance, gave the results shown in table 14.

Table 14. Reflecting power of the vane (per cent)

Left-hand side		Right-hand side		
Front end	Rear end	Front end	Rear end	Mean
70·7	66·3	62·2	62·8	65·5
65·4	66·6	62·7	64·4	64·8
67·3	64·4	63·0	67·6	65·6
67·7	65·3	61·6	63·9	64·6
69·1	65·5	61·4	63·1	64·8
			Final mean	65·0

Observations* (2): *measurement of the intensity of the radiation. These determinations were carried out on the completion of the deflectional observations in the manner which obviated the necessity for a separate evaluation of the energy loss due to the flask. In dismantling the latter the two portions of the flask surface, one on each side which had been traversed by the radiation, were cut out. These pieces were in turn placed in front of the radio-balance, at a distance approximately equal to the radius of the flask, while the intensity of the radiation was being measured.

Table 15. Intensity of radiation: radio-balance readings (μW. per 0·03467* cm.^{2})

Beam	Portion of flask interposed		Mean
	Left-hand side	Right-hand side	
1	2128 2113 2137	2099 2126 2104	2118
2	3135 3150 3125	3130 3164 3128	3139
3	4375 4374	4308 4273	4332

* Aperture of radio-balance cups.

Some difficulty was generally experienced in setting the vane at right angles to the axis of the optical system. When the fibre was delicate the ultimate position of equilibrium of the suspension could be ascertained only after evacuation of the flask. Moreover a slight displacement was apt to occur when the flask was fused on to the exhausting-apparatus. Sometimes this could be corrected by letting in air, softening one of the connecting tubes, and turning the flask. In this particular experiment the vane was found to set ultimately in a plane deviating by about 15° from the required position. The obliquity of the light converts the relation (12), giving the radiation pressure, into the form

$$(1 + m)\, PAr' \cos\phi = c\theta,$$

l, b
r'

in which if l and b represent the length and depth respectively of the vane, the arm r' at which the resultant force operates is given by

$$\tfrac{1}{2}\,(l - b\sec\phi),$$

ϕ

where ϕ is the angle of incidence of the radiation. The cross-sectional area of the beam is calculated as before from relation (9). The value of $\cos\phi$ derived from the directions of the optic axis of the system and the normal to the concave mirror was found to be 0·962. The total correction involved raised the pressure by 8 per cent.† It should be pointed out that this value is a little ambiguous in that it would have been modified by any slight deviation from parallelism between the plane of the vane and the normal to the concave mirror, the adjustment of which was only done by eye estimation. Any such deviation would not however have affected previous measurements with the other vanes, in which cases the light was incident normally.

---

† These figures correspond to the zero orientation of the vane. The total correction factor for this position agrees with the mean of the factors for the displaced positions, in the case of a given beam, to about one or two parts in a thousand.

The results finally derived by the use of the alloy vane are as in table 16.

Table 16

Beam	Pressure (dyne/cm^2)	Energy-density (erg/cm^3)	Difference (per cent)
I	$21{\cdot}2 \times 10^{-6}$	$20{\cdot}4 \times 10^{-6}$	+ 4
II	30·5	30·2	+ 1
III	40·6	41·7	− 3

Distribution of energy in the spectrum. The distribution of energy in the spectrum of the radiation falling upon the various vanes is indicated in figure 13, in which the energy is given in arbitrary units. The curve was derived by means of a Hilger constant-deviation infra-red spectrometer provided with a rock-salt prism. A sharply focused image of suitable size was cast upon the slit by means of the optical projection system used for observation of the radiation pressure. To allow for any selective absorption due to the glass of the flask a piece of the flask used in the case of the alloy vane was inserted in the path of the beam in front of the spectrometer slit. The filament-brilliancy was the same as in the pressure experiments with the alloy vane. Since the lamp voltage adopted in the case of each of the vanes used was in the vicinity of 100, the curve given may be taken as representative of the quality of the radiation obtaining throughout the whole series of measurements. It will be seen that the wave-length for which the energy is a maximum is in the neighbourhood of $1{\cdot}2\,\mu$, while the bulk of the incident energy arises from the wave band 0·5 to $2{\cdot}2\,\mu$.

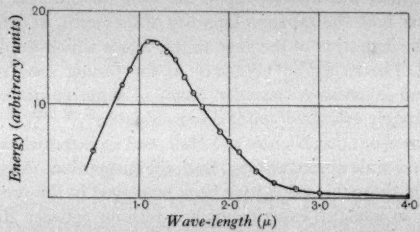


Figure 13. Distribution of energy in the spectrum of the radiation employed.

The method of varying the intensity of the radiation as required by altering the position of the lamp relatively to the rest of the optical system while maintaining the filament at constant brilliancy preserved the distribution of energy in the spectrum during the pressure and energy-measurements with any given suspension. Similarly the determination of the reflecting power of the vanes with the lamp voltages at the values obtaining during the deflectional readings avoided errors which might arise from the possible variation of reflection coefficients with the quality of the radiation.

Comparison of present experiments with those of previous observers. In comparing the experiments described with those conducted by earlier investigators, we must first direct attention to the work carried out by Nichols and Hull, whose results have hitherto been regarded as conclusive. The methods of measurement which they followed were in general considerably more complicated than those adopted in the present experiments. For example their calorimetric method of determining the radiation-intensity by measuring the rise of temperature produced in a metal disc entailed experiments which were indirect and lengthy in comparison with the use of a Callendar radio-balance for the same purpose. A further complication arose from the fact that Nichols and Hull's source of light was an arc lamp, difficult to keep steady for any length of time. This involved the introduction of an auxiliary bolometer by means of which the displacements of the suspension could be reduced to those which would be given by a lamp of standard intensity. Incidentally this correction, which in some cases was of the order of 50 per cent, involved the assumption that the radiation pressure was directly proportional to the intensity of the beam.

Since the radiation was directed upon the vane for only six seconds, it was necessary to reduce both the apparent intensity of the beam, as determined by the bolometer, and the deflection of the vane to the values which would obtain under static conditions. The reduction necessary in the former case was determined experimentally and involved a correction factor of some 50 per cent. The latter correction was wrongly evaluated and is discussed later.

It may be pointed out that Nichols and Hull used an extremely small deflection, namely 16 mm. on a scale distant 105 cm. from the suspension. Angular deflections up to about fifteen times this value have been employed in the present work.

In attempting to establish experimentally a relation between the pressure and energy-density of radiation it is of fundamental importance to derive a series of measurements covering as wide a range of radiation-intensities as possible. It is noteworthy that Nichols and Hull used what amounts practically to one intensity only. They give one final value for each of three different qualities of radiation, but the two extreme intensities involved differed by only some 8 per cent. Experiments we have conducted with the infra-red spectrometer lead us to doubt whether the quality of radiation obtained by Nichols and Hull by passing full radiation through red glass differed very greatly from the quality of the full radiation itself, unless the glass they used had special properties.

It is to be borne in mind that, when Nichols and Hull undertook their investigation, three modern advantages were not available to them, namely (*a*) exhaustion apparatus capable of producing a vacuum high enough to eliminate radiometer action; (*b*) a steady and powerful source of radiation; and (*c*) a quick and reliable instrument for use in connection with the energy-measurements. Nichols and Hull employed very elaborate and ingenious methods in the attempt to surmount these difficulties, but it is not to be expected that their indirect methods could give results so satisfactory as those obtained with more modern facilities.

Miss Golsen's work has not received much attention, possibly owing to the fact that Nichols and Hull's results have been generally accepted as quite conclusive. She worked only with metal vanes, whereas Nichols and Hull used silvered glass suspensions. Miss Golsen made an investigation of radiometer action with these metal vanes, and her general conclusions are in agreement with those given in this paper. For her radiation-pressure determinations she used balanced suspensions with the working surface on one side only of the stem. A range of radiation-intensities was, however, employed. The methods Miss Golsen adopted for the determinations of the energy of the beams, and for the measurement of the reflection coefficient of the vanes, were less direct than those in which a radio-balance is used. The possibility of errors of the order of ±6 per cent in the experimental work are admitted.

A comparison of the torsional constants of the fibres used in the investigations mentioned are given in table 17.

Table 17

Observers	Couple required to turn suspension through one radian (dyne-cm. $\times 10^{-3}$)	
Nichols and Hull	7·6	
Miss Golsen	1·1 to 4·0	
M. B.	Glass suspension	1·3
	Mica suspension	1·25
	Aluminium suspension	0·22
M. B. and S. E. G.	Alloy suspension	0·8

§ 4. ACKNOWLEDGMENTS

The authors are much indebted to the late Prof. H. L. Callendar for the interest which he took in this work. They also wish to record their grateful thanks to Mr W. J. Colebrooke and to Mr C. Hellary, of the Physics Workshop of the Imperial College of Science, and to Mr Baker, of Howard, Rawson and Co., for their help in the constructional work.

APPENDIX

Errors of calculation occurring in Nichols and Hull's work

In view of the great importance in modern physical theory of the relation of numerical equality between the pressure and energy-density of radiation, attention is directed to the experimental verification attempted by Nichols and Hull whose work has been widely quoted as the standard investigation in this connection. Stated by these observers as indicating agreement to 1 per cent between the pressure and energy-density, Nichols and Hull's results have hitherto been generally accepted as experimentally affording conclusive quantitative evidence of the validity of Maxwell's relation. Examination of the methods adopted by these investigators in deducing their results from their observations shows, however, the presence of considerable errors, inasmuch as corresponding values of pressure and energy-density for radiation of given intensity exhibit, when correctly evaluated, a divergence of some 10 per cent.

Working with a gas pressure of 16 mm. of mercury, Nichols and Hull did not directly observe the angle of displacement of their suspended system at which the couple due to the radiation pressure balanced that due to the supporting fibre. Nichols and Hull assumed that it was impossible to obtain a vacuum good enough to eliminate the disturbing influence of the residual gas surrounding their suspension. They therefore determined experimentally the pressure at which this radiometer action was a minimum, and made their observations at this pressure (16 mm.). Since gas action takes time to develop, whereas radiation pressure acts instantaneously, Nichols and Hull assumed that by keeping the radiation on the vane for six seconds (one quarter of the period of oscillation of the suspended system) gas action was eliminated, although at this pressure the gas caused the motion of the suspension to be heavily damped.

The procedure adopted was as follows. The suspension being initially at rest, the radiation was directed on the vane for one quarter of the periodic time of the suspension. On the removal of the beam, the vane continued to move towards a maximum displacement, which was observed. From this observed amplitude of the first swing of the suspension, the angle of displacement at which the couple due to radiation pressure would balance that arising from the torsion of the fibre could, assuming radiometer action to be negligible, be derived in the following way.

Throughout the interval during which the radiation is incident upon the vane the equation of motion of the suspension may be written

$$K\frac{\partial^2\theta}{\partial t^2} + 2\epsilon\frac{\partial\theta}{\partial t} + G\theta = L \qquad \ldots\ldots(1),$$

K, G ϵ where K and G represent respectively the moment of inertia of the suspension and the fibre constant, while 2ϵ is the damping factor, the assumption being made that the sole effect of the residual gas is to damp the vibrations. Since the constant L represents the torque due to the radiation, the angular displacement of the suspension, at which the couples arising from the radiation and the torsion of the fibre are equal, is given by L/G. The solution of the above equation of motion is

$$\theta = \frac{L}{G}\left[1 - e^{-(\epsilon/K)t}\sqrt{(1+x^2)}\cos(2\pi t/T - \delta)\right] \qquad \ldots\ldots(2),$$

x, T where $x = \epsilon T/2\pi K = \tan\delta$ and $T = 2\pi/\sqrt{(G/K - \epsilon^2/K^2)}$,

the values of the constants being determined by the initial conditions that θ and $\partial\theta/\partial t$ both vanish when $t = 0$.

Hence the values of the displacement and the velocity of the suspension obtaining on the removal of the radiation, after the lapse of time interval $\frac{1}{4}T$ from the commencement of the application, are given by the relations

$$\theta_{\frac{1}{4}T} = \frac{L}{G}[1 - e^{-\epsilon T/4K}.x] \qquad \ldots\ldots(3),$$

$$\left(\frac{\partial\theta}{\partial t}\right)_{\frac{1}{4}T} = \frac{L}{G}e^{-\epsilon T/4K}\left(\frac{2\pi}{T} + \frac{2\pi}{T}x^2\right) = \frac{L}{G}\cdot\frac{2\pi}{T}.e^{-\epsilon T/4K}.(1 + x^2) \qquad \ldots\ldots(4).$$

On the removal of the radiation pressure the equation of motion of the suspended system becomes

$$K\frac{\partial^2\theta}{\partial t^2} + 2\epsilon\frac{\partial\theta}{\partial t} + G\theta = 0 \qquad \ldots\ldots(5),$$

with the solution $$\theta = Ae^{-(\epsilon/K)t}(\cos 2\pi t/T - \alpha) \qquad \ldots\ldots(6),$$

in which the period T has the same value as before (24 sec. in the practical case), while the new zero of time is the instant of removal of the light. If r denotes the ratio of successive amplitudes of the damped vibrations of the suspension, then

$$\frac{\epsilon T}{2K} = \log\left(\frac{1}{r}\right) = \pi x.$$

The values of displacement and angular velocity given in relations (3) and (4) may be expressed

$$\theta_{\frac{1}{4}T} = \frac{L}{G}\left[1 - \frac{r^{\frac{1}{4}}}{\pi}\log\left(\frac{1}{r}\right)\right] \qquad \ldots\ldots(7),$$

$$\left(\frac{\partial\theta}{\partial t}\right)_{\frac{1}{4}T} = \frac{L}{G}r^{\frac{1}{4}}\frac{2\pi}{T}\left[1 + \frac{1}{\pi^2}\left\{\log\left(\frac{1}{r}\right)\right\}^2\right] \qquad \ldots\ldots(8).$$

These values determine the magnitude of the constants A and α in (6). Putting this relation in the form

$$\theta = e^{-(\epsilon/K)t}[X\cos 2\pi t/T + Y\sin 2\pi t/T] \qquad \ldots\ldots(9),$$

so that

$$\frac{\partial\theta}{\partial t} = e^{-(\epsilon/K)t}\left[-\frac{\epsilon}{K}\left(X\cos\frac{2\pi t}{T} + Y\sin\frac{2\pi t}{T}\right) + \frac{2\pi}{T}\left(Y\cos\frac{2\pi t}{T} - X\sin\frac{2\pi t}{T}\right)\right] \qquad \ldots\ldots(10)$$

and in each of these equations writing $t = 0$, we find from (7) and (8) that

$$X = \frac{L}{G}\left[1 - \frac{r^{\frac{1}{4}}}{\pi}\log\left(\frac{1}{r}\right)\right]$$

$$Y = \frac{L}{G}\left[r^{\frac{1}{4}} + \frac{1}{\pi}\log\left(\frac{1}{r}\right)\right].$$

Hence $$A = \sqrt{(X^2 + Y^2)} = \frac{L}{G}\sqrt{(1 + r)\left[1 + \frac{1}{\pi^2}\left\{\log\left(\frac{1}{r}\right)\right\}^2\right]} \qquad \ldots\ldots(11).$$

On insertion of the experimentally determined value of r, namely 0·783, derived by Nichols and Hull in the case of their suspension

$$A = 1{\cdot}339\,L/G; \text{ and since } X/A = \cos\alpha,\ \ \alpha = 0{\cdot}695 \text{ radian.}$$

From relation (10) the displacement θ has its maximum value when $t = 2{\cdot}77$ sec. Hence

$$L/G = \theta_{\text{max.}}/1{\cdot}260.$$

The angle at which the couple due to torsion of the fibre would, in the absence of radiometer forces, balance that due to radiation pressure is thus given as a fraction of the first amplitude of swing of the suspension.

Errors made by Nichols and Hull in (a) the evaluation of the radiation pressure

Adopting the general method of the analysis given, Nichols and Hull took the differential equation (1) as defining the motion of their suspension while radiation was incident upon it. Instead, however, of using the proper solution of this equation to obtain the position of the vane at any instant, they assumed the displacement θ to follow the relation

$$\theta = \frac{L}{G}\left(1 - e^{-(\epsilon/K)t}\cos\frac{2\pi t}{T}\right) \qquad \text{......(12).}$$

On this assumption the values of displacement and velocity respectively at time $\frac{1}{4}T$, the instant of removal of the radiation, are given by

$$\theta_{\frac{1}{4}T} = L/G$$

and

$$\left(\frac{\partial\theta}{\partial t}\right)_{\frac{1}{4}T} = \frac{L}{G}\cdot\frac{2\pi}{T}e^{-\epsilon K/4T}.$$

Under these circumstances

$$X = \frac{L}{G} \text{ and } Y = \frac{L}{G}\left[r^{\frac{1}{2}} + \frac{1}{\pi}\log\left(\frac{1}{r}\right)\right]$$

and hence

$$A = \sqrt{(X^2 + Y^2)} = \frac{L}{G}\sqrt{\left[1 + r + \frac{2r^{\frac{1}{2}}}{\pi}\log\left(\frac{1}{r}\right) + \frac{1}{\pi^2}\left\{\log\left(\frac{1}{r}\right)\right\}^2\right]}.$$

In their paper Nichols and Hull omit the term $\left\{\frac{1}{\pi}\log\left(\frac{1}{r}\right)\right\}^2$ as being negligibly small and give the value of $\sqrt{\left[1 + r + \frac{2r^{\frac{1}{2}}}{\pi}\log\left(\frac{1}{r}\right)\right]}$ as 1·357. Correctly calculated on the basis $r = 0{\cdot}783$, the figure given by Nichols and Hull, the value is 1·386. It appears that they have erroneously taken log $(1/r)$ to the base 10 instead of to the base e.

Having assumed the equation of motion of the suspension subsequent to the removal of the radiation to be

$$\theta = 1{\cdot}357\frac{L}{G}e^{-(\epsilon/K)t}\cos\left(\frac{2\pi t}{T} - \alpha\right),$$

Nichols and Hull make a further error in their deduction from this equation of the value of the first maximum amplitude of swing. Instead of deducing this from the time at which the angular velocity of the suspension has its first zero value, they have assumed that

$$\theta_{\text{max.}} = 1{\cdot}357\, L/G,$$

which is clearly incorrect since the heavy damping of the motion is ignored. Thus, while the true relation, giving the angle for which the couples due to the radiation and torsion of the fibre would balance, is

$$L/G = \theta_{\text{max.}}/1{\cdot}260,$$

Nichols and Hull used the equation

$$L/G = \theta_{\text{max.}}/1{\cdot}357.$$

Being proportional to L/G, their stated values of the pressure of the radiation are about 7·5 per cent too low.

It is to be noticed that the error would have been about 10 per cent if A had been correctly evaluated. The arithmetical miscalculation diminished to some extent the effects of the errors of analysis, namely, the adoption of an inaccurate equation (12) instead of (2) for the initial motion of the suspension, and the erroneous derivation of $\theta_{\text{max.}}$ in the last stage.

Errors made by Nichols and Hull in (*b*) *the evaluation of the energy-density.*

A further inaccuracy occurs in the estimation of the energy-density of the radiation. The method employed by Nichols and Hull to measure the intensity of the radiation involved the measurement of the rise in temperature produced in a metal disc by the incidence of the radiation. For the value of the mechanical equivalent of heat occurring in the calculation reference was made to Griffith's paper*. From this paper the value of J is wrongly quoted as being $4{\cdot}27 \times 10^7$ ergs per gram calorie, whereas the stated value is 427 gram-metres per gram calorie. Nichols and Hull have thus omitted to make the necessary conversion from gravitational to absolute units. The radiation-intensity values being proportional to the value of the mechanical equivalent, taking J to be 4·18 joules per calorie, have the effect of making Nichols and Hull's figures for the energy-density some 2 per cent too high.

Nichols and Hull's results as finally stated showed the values for the radiation pressure to be slightly greater than those for the energy-density by an amount of the order of 1 per cent. Allowance for the errors mentioned above in each case enhances the divergence, since an increase in the pressure is involved in conjunction with a decrease in the energy-density. It is thus seen that Nichols and Hull's results, when correctly calculated, show the pressure of radiation to be in excess of the energy density by some 10 per cent. Hence they cannot be regarded as furnishing conclusive quantitative evidence of the validity of the relationship of equality deducible from theory.

---

* *Phil. Trans.* A. **184**, 496 (1893).

It should be mentioned that in addition to the above there is considerable ambiguity in Nichols and Hull's paper regarding their use of galvanometers. In the course of their experiments they used two galvanometers G_1 and G_2. G_2 was in the auxiliary bolometer circuit which, as mentioned on page 348, was used to correct for variations of the intensity of the incident beam. G_1 was in circuit with the silver disc whose rise in temperature was employed to determine the energy density. The sensitivities of these galvanometers varied from time to time during the experiments, and therefore it was necessary to reduce all deflections of each galvanometer to those corresponding to the standard sensitivity of each instrument concerned. Nichols and Hull have nowhere defined what they mean by the sensitivity of a galvanometer, but in the following illustration* they have used an inverse definition in the case of G_1, i.e. they take the sensitivity to be the current required to produce unit deflection.

Example. The deflection of G_1 was 393·8 scale divisions for a temperature-range of 39·11 degrees when the sensitivity of galvanometer G_1 was 996. Nichols and Hull state that for a temperature range of 1 degree and with sensitivity of G_1 equal to 1000 a deflection of 10·03 divisions would be produced, i.e.

$$\frac{393{\cdot}8 \times 996}{39{\cdot}11 \times 1000} = 10{\cdot}03.$$

Thus they have used an inverse definition of sensitivity.

Nichols and Hull defined a standard light-beam as one, a constant fraction of which, when reflected into the auxiliary bolometer, would produce a deflection of 100 divisions on the scale of G_2, presumably, though they do not expressly state this, at a standard sensitivity of G_2. The example in table 6 on p. 588† shows that in the case of G_2 they have used the direct definition of sensitivity, i.e. the deflection per unit current. Thus when the energy was being measured, a beam which produced a deflection of 92·4 on the scale of G_2 (sensitivity 667) gave an observed rate of change of deflection on the scale of G_1 (sensitivity 996) of 1·307 mm./sec. The deflection which would be produced by the lamp on the scale of G_2 when at standard sensitivity, the direct definition being assumed, is 92·4 × 1000/667 divisions. The rate of change of deflection on the scale of G_1 at standard sensitivity, the inverse definition being assumed, is 1·307 × 996/1000 mm./sec. Hence the rate of change of deflection of G_1 produced by the standard beam would be 1·307 × 996 × 667 × 100/1000 × 1000 × 92·4, or 0·94 mm./sec.

The above expression is given by Nichols and Hull. All the results on table VII, p. 589† are similarly deduced. (A decimal point has evidently been omitted all through column 3, table VII.) Thus their results are only consistent if we suppose that in this set of calculations they have used two different definitions of the term "galvanometer-sensitivity."

Again the pressure values finally obtained on p. 581† are consistent with the direct definition of galvanometer sensitivity in the case of G_2, though the order in which these values are worked out on pp. 580–581* might at first lead the reader to think that these results were obtained by the use of an inverse definition but were miscalculated.

---

* *Proc. Amer. Acad.* **38**, 587 (1903).

† Nichols and Hull's paper.

Thus throughout their work Nichols and Hull's results are only consistent with the adoption of an indirect definition of galvanometer sensitivity in the case of G_1 and a direct definition in the case of G_2. The use, without explanation, of the same term with two different meanings, particularly when occurring in the same numerical expression, introduces complexity into a paper already rather difficult to follow.

It is of interest to observe that if Nichols and Hull had intended to use the usual direct definition throughout, their results would not have been very seriously affected, as the stated sensitivity of galvanometer G_1 was almost of standard value. If, on the other hand, they meant to use always the inverse definition of sensitivity, their stated values of pressure and energy-density would in each case be increased by more than 100 per cent.

At the same time, owing to the fact that the sensitivity of G_2 varied somewhat in the two parts of the experiment, the energy-density values would be increased by about 8 per cent more than the pressure values. This would offset to some extent the divergence between the pressure and energy figures consequent upon the errors of calculation mentioned earlier. However, the absence of precise information regarding the galvanometer-sensitivities renders suppositions such as the above no more than speculative.

DISCUSSION

Dr G. D. West. This paper has been of much interest to me. First, it has administered a mild mental shock. The pressure of light is involved in many physical and astronomical calculations, and hitherto one imagined that it was measurable to 1 per cent. To learn that a quantity so important has, up to now, been measured only to 10 per cent is disquieting. Nichols and Hull did their experiments when our modern vacuum technique was unknown. The pressure of light certainly needs remeasuring with modern apparatus, and I am glad that the authors have taken the matter in hand.

Reading through the paper, one forms the impression that the disturbing gas-action effects are as troublesome as ever. How troublesome they can be I found out some years ago when I made approximate measurements of the pressure of light by allowing a beam to fall on a strip of gold leaf in a test tube. The gold leaf is very light and thin and is deflected by an easily observable amount. There is no appreciable temperature-difference between the surfaces, and one might expect only a negligible radiometer effect. Gas-action effects of an entirely different kind appear, however, and these I subjected to a considerable investigation†. I think the authors would do well to study radiometer effects more generally, and apart from the vagaries of a particular instrument.

---

* Nichols and Hull's paper.

† *Proc. Phys. Soc.* **31, 32, 33.**

The question of the evolution of adsorbed gas might perhaps be given more prominence. Each molecule as it is emitted gives a reactive kick, and this of course disturbs the measurements. I should like to ask the authors if they are entirely satisfied with the explanation, based on reradiation, that they give of the results in table 3?

Mr G. G. Blake (communicated). On page 323 the authors give 10^{-6} mm. as the pressure at which gas action vanished. Would it not be well to make it quite clear that these figures only apply in the case of a radiometric vane the two faces of which are equidistant from the walls of a spherical containing vessel? Dr G. D. West* has shown that if a strip of aluminium foil is suspended near to one side of an evacuated vessel, instead of centrally, it is, when irradiated, deflected away from that side of the vessel independently of the side of the strip upon which the radiation falls.

In June last year whilst conducting some experiments with a "radiometric condenser†" I employed a thin leaf of aluminium foil to act as the variable plate of a condenser. Both this leaf and a rigid back plate in close proximity thereto were enclosed in an evacuated vessel and employed to control the frequencies of a zero-shunt thermionic valve circuit; the movements of the leaf were then magnified and registered with aid of a galvanometer in the plate circuit of the valve. The glass vessel containing the condenser was exhausted for me by the courtesy of the G.E.C. Research Laboratories to 10^{-7} mm. Incident radiations caused very good excursions of the leaf (when thus magnified) away from its back plate towards the source of radiation. Exhaustion was not carried beyond this value, but certainly we had not nearly reached the limit for this particular radiometric arrangement.

The illustrations of the apparatus employed by the authors do not show any heat-filters between the source of radiation and the radiometer. Is it not possible that the reluctance of the vane to return to zero, mentioned on page 332, may be due (at any rate partially) to increased temperature of the wall of the radiometer flask, on its side nearest to the incident radiation? A repetition of a few of the observations with the radiometer flask protected from the heated atmosphere by means of a Dewar flask might yield different results. In any case the protection of the walls from changes in atmospheric temperature would appear to be advisable. On page 333 it is interesting to compare the figures given by the authors with those given by G. D. West for maximum thermokinetic effects. The authors give 10^{-2} to 10^{-3} mm., and West gives 2×10^{-2} mm. for his radiometric aluminium leaf.

Authors' reply. It is to be strongly emphasized that the observed gas effects, which were perfectly definite and reproducible, apply only to flat rectangular vanes suspended by means of a quartz fibre, centrally, within a spherical glass vessel. The experiments were repeated several times with flasks of different diameters, and the results were always as indicated. The dimensions of the flask were, however, purposely always made great compared with those of the vane, in order to minimize any possible effect due to the proximity of vane and walls. The experiments of

---

* *Proc. Phys. Soc.* **28** (1916).

† *Elec. Rev.* **112**, Jan. 13 (1933).

Mr Blake and Dr West appear to have been widely different: for instance Dr West used gold leaf in a test tube. Divergences in observed effects were therefore to be expected.

In reply to Dr West: The impression that disturbing gas effects were as troublesome as ever is erroneous. One of the purposes of the present paper is to show that with thin metal vanes, at a pressure of 10^{-6} mm., radiometer action was entirely eliminated.

In tables 6 and 11 it is seen that, with these vanes, the conditions of vibration conform exactly to those stipulated in the last two paragraphs on page 323 of the paper. We consider that we have here clear experimental evidence that radiometer action is absent. This evidence is rendered complete when the results given in figure 12 and discussed on page 343 are considered. The question of adsorbed gas is dealt with on page 334. In the course of a long series of observations we recollect only one occasion when a sudden jerk in the deflection implied the emission of gas from the surface of the vane. With regard to the point about reradiation, as is indicated in the paper (page 330) this is merely a suggestion, but reradiation appears to operate in the right direction. We hope to undertake some more work in this connexion, as further experimental data are required.

The first part of Mr Blake's criticism has already been dealt with. It should have been mentioned in the paper that, throughout the observations, the flask was protected from draughts and extraneous radiation by a thick asbestos jacket with suitable openings for admitting the radiation and studying the deflections. It is not easy to see how the slightly increased temperature of the wall of the flask, adjacent to the source of radiation, could produce the regular zero-lags observed. These lag effects and also the initial variation of the deflections with glass vanes (tables 2 and 4) can be explained if it is assumed that the pressure due to true radiometer action (page 333) is gradually counterbalanced by a lowering of the density on the hotter side of the vane; and that similarly, when the radiation is removed, the radiometer action dies away before the density again becomes uniform. If it is remembered that the blackened or platinized film is always the hotter side of the vane, the initial variation of the deflections (tables 2 and 4) when the radiation is first applied, and the direction of the residual deflections (zero lag) when the radiation is removed (table 5), can be readily understood.

REVIEWS OF BOOKS

Faraday's Diary: being the Various Philosophical Notes of Experimental Investigation made by Michael Faraday, D.C.L., F.R.S., during the years 1820–1862. Vol. 1 (Sept., 1820–June 11, 1832), pp. xxiii + 430; vol. 2 (Aug. 25, 1832–Feb. 29, 1836), pp. xvii + 467. (London: G. Bell and Sons. To be completed in seven volumes.) Price twelve guineas the set.

The *Diary*, which was bequeathed by Faraday to the Royal Institution, is published under the editorial supervision of Mr T. Martin. The Foreword is by Sir William Bragg, who has already published—some months ago—an admirable summary of the chief features of the *Diary*.

There are diaries of many kinds, and it would be difficult to imagine anything sharper than the contrast between this of Faraday and that—also posthumously published—of one of his remotest predecessors in the Fellowship of the Royal Society. Faraday's *Diary* is above all else a record of his day-to-day work in the laboratory of the Royal Institution and—what is vastly more important—of the ideas which were continuously inspiring him to this work. Read in conjunction with the perfected accounts in the volumes of *Experimental Researches*, it tells us of Faraday as a scientist everything that can well be conveyed by the printed word. But of Faraday the man, his personal affairs and his personal relations, it tells practically nothing at all.

We do find, it is true (para. 1503) a reference to a visit by Daniell to the laboratory, coupled with a cordial appreciation of Daniell's generosity in a matter of scientific priority—but personal references of this or any sort are extremely rare. This is not, however, to say that the *Diary* lacks human interest. It would be difficult for anyone, however slight his familiarity with the normal routine of life in the laboratory, to read these pages without forming a vivid picture of Faraday at work, of his attitude in the face of difficulties and his reactions to a success or a temporary check. The *Diary* is illuminating in minor details of Faraday's work as well as in the main lines of his researches; take, for example, this almost trivial detail (para. 1941) with reference to the design of a new voltaic battery which was to replace the one already in use: "Must have a plug at the corner of trough to withdraw the acid by." It is by such notes as this that we realize some of the difficulties under which experimental work was prosecuted a century ago—namely, how many types of apparatus, now accepted as commonplace furnishings of even the worst-equipped laboratory, had then to be specially designed for the work in hand. When it is remembered in addition—and this point is not brought out in the *Diary*—how much of Faraday's time was absorbed in routine duties and in Government work on optical glasses, it becomes even more difficult to express in finite terms a proper appreciation of his intense scientific activity during the period covered by these two volumes (1820–1836).

The *Diary* will necessarily and strongly appeal to all—and not only to chemists and physicists—who would like to know more of the processes by which a great experimental philosopher arrived at the results which have had such far-reaching importance, not only in the history of scientific thought, but in the whole of our social and industrial life. These volumes should do much to stimulate a greater interest in the history of scientific discovery—a service particularly necessary at a time like the present, when, in Physics at least, so much of the older work, in spite of its beauty and elegance, is sadly out of fashion.

Mr Martin's editing has been both pious and scholarly. There has been a minimum of interference with Faraday's wording and punctuation, and the placing of the diagrams in relation to the text follows the original as far as is practicable on the printed page. The cross references which have been inserted (from the *Diary* to the *Experimental Researches*) are a particularly useful piece of editorial work.

The reproductions of Faraday's line drawings, which form an essential part of the *Diary*, deserve a word to themselves. It is conceivable that a professional art critic could trace in the drawings some indication of the teachings of J. J. Masquerier, but to the untrained eye—if this may be said, with all due reverence—they do not differ appreciably in conception or execution from the pictures which most of us draw on blackboards, in rough note-books, and on the blotting-paper provided at meetings. They are all the more delightful on this account, for at least in this one insignificant respect they bring Faraday into closer fellowship with the humblest of his followers. They have been slightly reduced in size for printing, and the reproduction and placing have been performed with conspicuous skill and taste.

Faraday's services to the Royal Institution are matters of old and well-known history. The many demands for his professional services gave him opportunities for acquiring wealth on a scale which might have tempted even men who were far less familiar than he was with poverty. It was not solely his passion for unfettered research which determined his refusal of these demands—it is certain that his conception of his duty to the Institution which sheltered his researches was a very important factor. It is proper to recall here also his possibly over-sensitive pride in the special position of the scientific pioneer—a feeling which made him averse to such forms of public or official recognition as were the common rewards of success or eminence in other spheres.

It follows therefore that perhaps the most fitting of all memorials to Faraday and to the survival of his ideals is to be found in the continued activity of the Royal Institution and its Davy-Faraday Laboratory in the winning and dissemination of new knowledge. In ordering the publication of his *Diary*, the Managers of the Royal Institution have paid to his memory a very appropriate and a more definitely personal tribute. If, in so doing, they have liquidated some part of the Institution's debt to Faraday, they have at the same time done a service to science and scientific history which we are glad to acknowledge here.

H. R. ROBINSON

Wave Mechanics: Elementary Theory, by J. Frenkel. Pp. viii + 278. (Oxford: Clarendon Press.) 20*s*.

This volume, although intended to be the first of three, is complete in itself. It takes the form of a survey of the subject, leaving advanced mathematical methods for the second volume, and details of the applications to the third.

Its scope, then, is practically identical with that of a number of one-volume accounts of wave mechanics recently published, in that they all consist of an introduction, but only an introduction, to the whole subject. It is in the early part of these books, the justification for assuming a wave-corpuscle parallelism both for light and for matter, that the main divergencies in treatment occur as between different authors.

Frenkel's outlook has returned more closely to the original one of de Broglie than is now usual, although he goes even further in some ways than de Broglie himself. After an illuminating investigation of Newton's corpuscular theory of light, in which appeal is made in a distinctly un-Newtonian manner to the principle of conservation of energy, he proceeds to sketch the underlying ideas of the modern relativity theory, and from this develops Einstein's theory of light darts.

The argument for wave mechanics, summarized, is based on the relativity relations (1) momentum g of a particle $= mv$ and (2) its energy $E = mc^2$, where m is the mass and $= m_0/(1 - v^2/c^2)^{\frac{1}{2}}$, v is the velocity of the particle, and c is the velocity of light. Now if

$v=c$, and the mass is not infinite, then m_0 must vanish, so that particles of zero rest-mass could only exist when moving with the speed of light. Consequently, if they exist at all, they must be corpuscles of light, as is indeed suggested by certain properties of light. For them, the general relation $g=Ev/c^2$ reduces to $g=E/c$. Now from interference and other experiments we are convinced that a wave-length λ is associated with any beam of light, and we are in the habit of defining a frequency ν by the relation $c=\nu\lambda$. If, now, the energy E depends only on the frequency or wave-length, then the relativity condition of covariance shows that the relation between them must be $E=h\nu$.

We may profitably examine this argument in closer detail. E is the energy of an individual corpuscle—photon, let us say—and it cannot depend either on the velocity or on the rest-mass, since each of these is the same for all photons. Consequently it can only be a function of λ, or (what is essentially the same thing) of ν. This is the statement in the book under review, and it has the merit of appearing rigorous, and of showing that the relation $E=h\nu$ is inevitable on logical grounds, without any need for an appeal to experiment. It is easy to see, however, that there is a lacuna which, according to taste, may be either supplied by the reader or regarded by him as one loophole which will remain open for the construction of yet a new theory when, if ever, wave mechanics comes to need a successor. The possibility which is overlooked is that the energy per corpuscle might depend on the number present. This would be the case, for example, if photons were able to influence each other gravitationally or magnetically.

To return to Frenkel's argument. It is pointed out that the equations $E=h\nu$ and its companion $g=h/\lambda$ remain formally true even for particles with a finite rest-mass if a quantity λ and a quantity ν are associated with them, so that it is justifiable to take the step of associating a wave, not indeed with a single particle, but, as in the case of light, with a whole stream of identical particles all having the same momentum and the same energy. If it is assumed that the square of the amplitude of the wave so introduced is proportional to the particle density, then the only step which remains is to assign a physical reality to the wave which already has full mathematical justification. The relations previously quoted are sufficient to find the wave velocity, and to show that there is dispersion and hence a group velocity, which is identified with the particle velocity.

This part of the book has been treated in considerable detail, because it puts the matter in a neater form than most accounts have been able to do. It is, in fact, concerned to show that the fundamental ideas of wave-mechanics are inevitable, whereas writers have generally been concerned (or at any rate able) to make them plausible.

It is to be noted, moreover, that the train of reasoning used imposes a principle of indeterminism, in the sense that the exact position of discrete particles cannot be deduced if only their mean number per unit volume is specified by a continuously distributed quantity, the wave amplitude.

After the development of these ideas, the experiments which have shown the "wave" aspect of electrons and of atoms are briefly described, but the outlook is not that of the experimentalist and but little weight seems to be attached to these mere verifications of a theory which has been established on quite other grounds, and really requires no verification.

As has been mentioned above, the principle of indeterminism is based here, in the first place, on the necessity of allowing a simple harmonic wave to represent a whole stream of similar particles—or rather, copies of one particle, since there is no interaction between them. When the motion of a single electron is to be studied, it is natural to replace the average number per unit volume by the probability of finding the single one in the volume element concerned.

Incidentally, the facts of partial reflection and partial transmission of a beam of a light at an interface between two media, requiring some photons to move one way and some another, are likewise well explained by a probability interpretation. The analogy between this behaviour and the "fits of easy reflection" and "fits of easy refraction" to which Newton's corpuscles were subject is striking and is well brought out by Frenkel.

The point of view from which Heisenberg approaches the uncertainty principle is set forth in detail, but the author is unsympathetic to it, considering that the part played by the experimenter is stressed too much. He maintains that since all measurements must alter the quantity observed (e.g. in the case of temperature-measurement, conduction by the thermometer or thermocouple enters into the question), therefore the imaginary γ-ray and other measurements cited by Heisenberg do not undermine our faith in determinism by the mere fact that they alter the quantities to be measured. In his view, Heisenberg's argument merely brings out the indeterminacy already fundamentally accepted in the course of the discussion. The difference between these and "classical" experiments is that in the latter the alterations caused by the observation itself can be corrected for; in wave-mechanics they cannot, and this is because of the underlying lack of determination. In his own words "the application of this principle to the phenomena of the motion of elementary particles does not lead to indeterminism...but *simply reveals the indeterminism which is pre-existing in these phenomena*...."

It is interesting to notice that one of the arguments which has been much used by some writers as a reason for our belief in indeterminacy is hardly even mentioned by Frenkel, viz. the argument that since a wave-packet of finite dimensions must (by ordinary mathematical reasoning) spread as time goes on, therefore the position of the particle which it represents becomes more and more indefinite with the passing of time.

The following section introduces the quantum conditions, illustrated by the motion of an electron in a closed space, so that its associated wave is a stationary one with nodes at the boundaries of the space. This leads up to the formulation of Schrödinger's wave equation, with a further dissertation—an interesting one—on the probability interpretation.

Roughly half the book is devoted to the problems of the single particle in various fields of force, together with the discussion of the philosophical basis of the whole theory. This first half contains, in addition to what has already been discussed, a development, mainly on orthodox mathematical lines, of the theory and its applications to the hydrogen-like atom, the linear and spacial oscillators, the rotator, a very simplified type of crystal lattice and other problems. The "leakage" of particles past a barrier or valley of potential, first discovered in connexion with radioactivity, is applied also to explain the Ramsauer effect and the extraction of electrons from a cold metal by an electric field. Incidentally, the method of replacing the graph of a complicated potential function by an approximation consisting of straight lines is dignified by the name of the Potential Staircase Method.

An important matter is the case where two frequencies are present in the wave function of an electron in an atom. As is well known, these "beat" with the frequency of the light emitted in a Bohr transition from the state associated with one of them to the state associated with the other. In 1924 or 1925, Schrödinger believed that this indicated a fluctuation of a physical charge-density, leading by classical electrodynamics to the emission of light with the frequency of the fluctuations. It is pointed out that this conception cannot be incorporated into wave mechanics with a probability interpretation, because the fluctuations are then definitely debarred from being pictured as movements in a physically real charge-distribution. The author reaches the conclusion that "the important point is not to mix corpuscular conceptions with wave conceptions....If matter is to be described in corpuscular terms...then light must also be described in corpuscular terms, and light-emission visualized as the emission of a photon. If, on the other hand, we wish to describe light-emission as the spreading of electromagnetic waves, then the electron must likewise be described as a wave system." Actually the author makes no secret of the fact that he regards the wave picture as definitely superior, both for light and for matter.

No space has been left to discuss the second half of the book, which deals first with the wave mechanics of a system of particles, and then, proceeding via Pauli's exclusion principle and the properties of symmetric and anti-symmetric functions, with that form of statistical mechanics which is found to be appropriate to wave mechanics. It will be found interesting to read a very lucid paper by Brillouin* in connexion with this chapter, since they are in some respects mutually complementary.

The last chapter differs from the rest of the book not only in subject-matter but in style. It was written after the proofs of the rest were completed, and is in a sense a foretaste of the third volume. It deals with the applications of quantum statistics, chiefly to the properties of metals, and contains a certain amount of original matter but no answer to Fowler's question† "Why is a metal?"

J. H. A.

Short Wave Wireless Communication, by A. W. LADNER, A.M.Inst.C.E., and C. R. STONER, B.Sc., A.M.I.E.E. Pp. xii + 348, with 13 plates and 201 text figures. (London: Chapman and Hall, 1932.) 15*s*.

This is a very useful general review of the methods and problems of radio communications using wave-lengths less than 150 metres. That it is mainly concerned with the Marconi systems is natural in view of the experience of the authors and, although this does not lead to the exclusion of some reference to other systems, the fact might in the next edition be recognized in some such sub-title as "with special reference to the Marconi systems." It has all the merits and some of the defects of a text-book which has grown from lecture notes; the diagrams are blackboard diagrams, and the authors sometimes forget that they are no longer beside the blackboard to lighten its darkness. Figures 54, 58, 60, 85 and 120 are typical of the cases in which exposition is inadequate or misleading, labels of ordinates and scale values are missing, and so on. The authors have learned that repetition is a virtue in teaching, and have not been afraid of it, but it is doubtful whether the degree of colloquialism and anthropomorphism which is permissible in the lecture room is appropriate to the printed page. It is, for example, hardly fair to the reader to say (p. 94): "Actually no intelligence can be conveyed by a single side-band system unless (*a*) The receiver knows what intelligence it is to expect...." There is, too, a certain carelessness about proper names ("Delinger," p. 67, and "Vigoreaux," p. 173, for example), about units (microvolts per metre are not the appropriate units for internal noise-levels, kilocycles are not units of frequency), and about good English ("flick impulsing," p. 118, is an unhappy addition to technical vocabulary, and "parasites" *tout court*, p. 146, are irritating...). As a last item in this critical paragraph we would protest against this statement: "The name 'push-pull' is given to those circuits impulsed by two valves arranged differentially. Of course it is not necessary to employ two valves to obtain a push-pull action.... " This may be true, but in this shape it is not good for students.

But when all this has been said we must repeat that we like the book, and we may cite the chapters on high frequency feeders, aerial arrays, commercial receivers, commercial transmitters, and ultra short-waves, and the paragraphs on Eckersley-Tremellen Charts as especially interesting sources of data not conveniently available elsewhere.

Optische Abbildung: Einführung in die Wellen- und Beugungstheorie optischer Systeme, von Dr JOHANNES PICHT. Pp. x + 243, with 65 figures. (F. Vieweg und Sohn, Brunswick, 1931.) Paper covers, RM. 20; bound, RM. 22.40.

Dr Picht has been engaged in recent years in carrying out an extensive detailed investigation of the properties of images formed by optical systems according to the wave theory of light. Although the physical principles to be employed are simple, the examination of the light-distribution in the image space in the presence of aberrations inevitably involves somewhat elaborate mathematical expressions. Those who are interested in the subject should certainly consult this book, which summarizes much of the work already done. The fact that some numerical results are presented in graphical form will be particularly appreciated by those who do not care to follow the more general investigations. We miss references to somewhat similar work published in this country.

---

* *Annales de Physique*, 7, 315 (1927).

† *Proc. Phys. Soc.* **42**, 458 (1930).

Grundlagen der praktischen Optik: Analyse und Synthese, optische Systeme, von Dr M. Berek. Pp. vii + 152, with 63 figures including one plate. (Walter de Gruyter und Co., Berlin, 1930.) RM. 13.

A large part of this book is devoted to the exposition of general optical laws and of methods of calculation such as form an important feature of a number of German optical books. It differs from some others in presenting and applying the convenient thin-lens formulae obtained by Airy and others which became widely known through such books as Coddington's and Dennis Taylor's. In addition a system of equations is given for the direct solution of triple photographic lenses, which is claimed to be simpler than the systems of some other German writers. These equations only cover the first-order aberrations of thin lenses, and no guidance is given for systems of more than three lenses. Numerical examples are included, but the discussions throughout are confined to well known systems. The book is reasonably indexed and a table of symbols and their meanings is included.

Atomic Energy States, by R. F. Bacher, Ph.D., and S. Goudsmit, Ph.D. Pp. xiv + 562. (New York and London: McGraw-Hill Publishing Co., Ltd.) 36*s*. net.

Since the appearance of A. Fowler's *Report on Series in Line Spectra* and Paschen and Götze's *Seriengesetze der Linienspektren* in 1922, great progress has been made in the theory and analysis of atomic line spectra, and several important books on certain aspects of the subject have been published, such as Hund's *Linienspektren und Periodisches System der Elemente* (an English translation of which should certainly have been published in 1926 or 1927), Grotrian's *Graphische Darstellung der Spektren* in two volumes, Pauling and Goudsmit's *The Structure of Line Spectra*, and Ruark and Urey's *Atoms, Molecules and Quanta*. The last two of these belong to the International Series to which has recently been added the volume now reviewed. An adequate idea of the enormous output of papers on atomic spectra in this period can only be obtained by perusal of the extensive bibliography accompanying Gibbs's review, *Line Spectra of the Elements*, the first part of which appeared last year in *Reviews of Modern Physics*.

Of the works mentioned, none but Bacher and Goudsmit's supplements the 1922 tables of Fowler and Paschen-Götze with a new compilation of complete numerical data. In the present work we find extensive tables giving the classifications (symbols, electron configurations, etc.) and numerical values of the known terms for all the atomic emitters, neutral and ionized, arranged in alphabetical order, from neutral A to trebly-ionized Zr. These tables, with brief notes at the head of each, occupy no fewer than 519 of the 562 pages; many pages, it is true, are less than half-filled, thus allowing useful space for the reader to add new data as they appear in the journals. In an introduction of 21 pages an adequate account is given of such results of atomic spectrum theory (e.g. electron configurations, couplings, selection rules, etc.) as are necessary for the understanding of the notation and the construction of the tables. The tables, unlike those of Fowler and Paschen-Götze, do not include wave numbers of observed lines; to obtain an idea of the spectrum of a given emitter from the relevant table of term values, the reader must apply results summarized in the introduction. A very welcome and useful inclusion near the end of the book is Paschen's 1928 tables of Rydberg terms $xR_\infty/(m+a)^2$, with x equal to 1, 4, 9 and 16.

The compilers have wisely avoided mention of any notation but the one now in general use for atomic spectra. This is in pleasing contrast to the rather unnecessary inclusion in some other recent spectroscopic works of detailed discussions of the two notations and empirical systems of numeration which served adequately ten years ago but have now given place to those used in this volume.

The printing work is excellent throughout. It may be pointed out, however, that $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$ appear on page 6 for ½, 1½, 2½. Again, English readers are hardly accustomed to the placing of the decimal point at a lower, rather than a higher, level than a dot used as a sign of multiplication; thus the familiar form "$h=6{\cdot}547 . 10^{-27}$" or "$6{\cdot}547\times 10^{-27}$" appears as "$h=6.547\cdot 10^{-27}$," and so on throughout the book.

The tables are very well arranged, and the introductory chapter is clear and logical apart from the fact that the expressions "equivalent electrons," "dipole radiation" and "quadrupole radiation" are used without explanation or definition. Many of the sentences are unnecessarily involved and inelegant on account of the excessive use of the word "one" (apart, of course, from its necessary occurrence as a numeral) as in the following passages:

p. 5: "one places the electrons in order of their n, and for the same n in order of l. For many electrons one usually gives the symbols for only the outermost ones.... When the arithmetical sum of all the l's of the electrons is *even*, one obtains *even* energy levels; and, in the other case, *odd* ones."

p. 11: "...if one considers two electrons, one in a low energy state and the other in a highly excited state, the spin-orbit interaction of the first may be larger than its interaction with the second one. If one now brings the second electron.... In such a case low states will show Russell-Saunders coupling; higher ones will not."

Similarly, on pages 3 and 6 "each one of" and "the ones" are used for "each of" and "those" respectively.

These minor blemishes, however, will in no measure detract from the very great value of the work to the active spectroscopist; to him, indeed, it is well-nigh indispensable. It will be used to best advantage in connexion with other works, such as Grotrian's second volume, Pauling and Goudsmit's book and Gibbs's bibliography.

W. J.

Annual Tables of Constants (*A.T.C. and Numerical Data*). (Paris: Gauthier-Villars et Cie.) Vol. **8**, part 2, 1927–1928. Pp. xxi + 1604. 500 fr. Parts 1 and 2. Vol. **9**, 1929. Pp. l + 1607. 400 fr. Index to vol. **9**.

Physicists need no introduction to the volumes which mark the progress of Dr Marie's great enterprise. With the increase in output of scientific research has come a corresponding increase in the dimensions of the *Annual Volumes*, and now the data of vol. 8, part 2 (for 1927–1928) and vol. 9 (for 1929) are contained in two massive volumes which together turn the scale at nearly 18 pounds' weight. But the editor, realizing that a guide to this labyrinth is very necessary, has provided an admirably arranged *table des matières* to vol. 9, which considerably reduces the time and trouble of running down a particular figure.

It is impossible, and undesirable, to give a detailed review of the contents of these weighty tomes. It is sufficient to say that the reviewer has tested this immense mass of chemical, physical and biological data at various points, and has nowhere found the desired information wanting, or over-difficult of access. The tables are indispensable to all serious researchers, and it is by no means one of their least merits that the publication is produced at a price which brings them within the reach of individual workers.

A. F.

Photograms of the Year 1932, edited by F. J. MORTIMER, Hon.F.R.P.S. (London: Iliffe and Sons, Ltd.) Paper covers, 5*s*.; cloth bound, 7*s*. 6*d*.; half-bound leather, 10*s*. 6*d*.

Photograms of the Year provides a very useful standard by which the amateur in photographic art may learn to assess his work. A series of more than eighty beautifully reproduced photographs affords ample practice for the study of grouping, of balance, of chiaroscuro and of choice of subject.

The value of the book is enhanced by an article from Mr C. J. Symes commenting critically on the pictures reproduced in the volume, and by a summary of the year's work written by the editor.

A. F.

THE PROCEEDINGS OF
THE PHYSICAL SOCIETY

VOL. 45, PART 3 *May* 1, 1933 NO. 248

551·594·11

RELATIONS BETWEEN THE COMBINATION COEFFICIENTS OF ATMOSPHERIC IONS

BY F. J. W. WHIPPLE, Sc.D., F.INST.P.

Received December 12, 1932. *Read February* 3, 1933.

ABSTRACT. The principal object of the paper is to put forward for consideration a formula,

$$\eta_{12} - \eta_{10} = 4\pi e w_1,$$

which indicates that the combination coefficient η_{12} for small ions and large ions of the opposite sign exceeds the coefficient η_{10} for small ions and uncharged nuclei, and further that the difference between the two coefficients depends on the mobility w_1 of the small ions. The experimental evidence for the formula is discussed, as well as possible applications.

§ 1. INTRODUCTION

In the theory of the conductivity of the atmosphere, rates of combination of ions are of great importance. These rates are difficult to determine and it would be advantageous if the necessary observations could be simplified by the application of some new general principle. As long ago as 1902 Langevin investigated the relation between the rate of combination of ions and their mobilities; the ions in question were those produced by radioactive processes in filtered air. In atmospheric electricity such ions are known as "small ions," to distinguish them from the large ions of small mobility. As a limiting case in his theory Langevin found a formula which would hold if every close approach of two small ions of opposite sign led to a combination. His experimental investigation demonstrated that the formula was not satisfied for air at atmospheric pressure, but it became a good approximation at higher pressures.

By using Langevin's method we can obtain similar formulae involving the combination coefficients which determine the rates of combination of small ions with large ions and with uncharged nuclei. The new formulae appear to be in accordance with experimental data. Though it is true that these data are too scanty to establish the validity of any general theory, the verification is satisfactory as far as it goes.

Some tentative applications of the new formulae have been made. For example the question whether the proportions of charged and uncharged Aitken nuclei in the air vary systematically is discussed. At the end of the paper the variation of the combination coefficients in air which is kept stagnant a long while is considered, and evidence is quoted to show that the combination coefficients for small ions and uncharged nuclei increase in the same proportion as the areas of the individual nuclei.

§ 2. NOTATION

The following notation will be used.

N N is the number of Aitken nuclei per unit volume;
N_1 N_1 „ of large + ions (i.e. nuclei with + charges);
N_2 N_2 „ of large – ions (i.e. nuclei with – charges);
N_0 N_0 „ of uncharged nuclei;
n_1 n_1 „ of small + ions;
n_2 n_2 „ of small – ions;
w_1 w_1 the mobility of a small + ion, i.e. the velocity in a field of unit strength in the electrostatic system of units; and
w_2 w_2 the mobility of a small – ion.

The combination coefficient η_{10} is defined by the statement that the frequency of
η combinations of small + ions with uncharged nuclei is $\eta_{10} n_1 N_0$ per unit volume per
unit time. Similar definitions hold for η_{12}, η_{20} and η_{21}. The mutual combination
α coefficient for small ions of opposite signs is α.

It will be assumed that each of the large ions carries the single electronic charge e. This has been verified* by J. J. Nolan, Boylan and de Sachy who found that

$$N = N_0 + N_1 + N_2 \qquad \text{......(2·1)},$$

N and N_0 being determined by the Aitken nucleus counter, whilst N_1 and N_2 were
e measured electrically on the assumption that the charge on each ion was e.

In the notation adopted here, the formula suggested by Langevin is

$$\alpha = 4\pi e\,(w_1 + w_2) \qquad \text{......(2·2)}.$$

The new formulae which will be examined are

$$\eta_{12} - \eta_{10} = 4\pi e w_1 \qquad \text{......(2·3)},$$

and

$$\eta_{21} - \eta_{20} = 4\pi e w_2 \qquad \text{......(2·31)}.$$

§ 3. LANGEVIN'S EQUATION

The argument† leading to Langevin's formula is briefly as follows. If a positive ion is at A and a negative at B and there are no other ions at a distance comparable with that between A and B, then the ions will move straight towards each other. The force acting on each is e^2/AB^2 and the relative velocity is $(w_1 + w_2)\,e/AB^2$.

---

[*] *Proc. R. Irish Acad.* 37 A (1925).

[†] *Ann. de Chim. et de Phys.* **28**, 438 (1903). Cf. Sir J. J. Thomson and G. P. Thomson, *Conduction of Electricity through Gases* (3rd ed. 47, 1928). N.B. The α of the present notation is αe in Langevin's.

Since n_2 is the density of the − ions, the number of these crossing in unit time the surface of a sphere with centre A and radius AB is on the average,

$$4n_2\pi AB^2(w_1+w_2)e/AB^2 \quad \text{or} \quad 4n_2\pi(w_1+w_2)e.$$

There are n_1 positive ions like A in unit volume, so the number of close approaches in unit time is $4n_1n_2\pi(w_1+w_2)e$. If every close approach led to combination, then the combination coefficient α would satisfy the proposed relation,

$$\alpha = 4\pi e(w_1+w_2).$$

The term combination is used rather loosely here. The small ion is supposed to be formed of a chain or cluster of about a dozen molecules associated with an ionized atom of oxygen or nitrogen. Probably when two ions of opposite signs collide the ionized atoms recombine to make a molecule, and the clusters of molecules break up.

This summary of Langevin's argument is too much simplified. Whilst it takes account of the velocity of the ion due to electrical attraction, the velocity due to thermal agitation or Brownian movement is ignored. On account of this agitation the relative velocity of two ions will not in general be along the line joining them; they may approach one another but pass by without collision, each describing an arc of a hyperbola.

Experiments have shown that the formula is not valid for ordinary pressures. Langevin developed a method by which he could determine ζ, the ratio

ζ

$$\alpha/4\pi(w_1+w_2)e.$$

If the formula had always held, then the value of ζ would have been unity. Actually Langevin obtained* the following results:

Pressure (mm.)	152	375	760	1550	2320	3800
ζ	0·01	0·06	0·27	0·62	0·80	0·90

For low pressures ζ is nearly proportional to the square of the pressure. Since w_1 and w_2 are inversely proportional to the pressure, it is implied that α is proportional to the pressure. Langevin explains this by supposing that a preliminary to combination is a collision of one of the ions with a gas molecule when the ions are within a certain distance. The chance of such a collision is proportional to the pressure. For a pressure of five atmospheres the value of ζ was 0·90. It is likely that for higher pressures the approximation to unity would be much closer. I do not know if the appropriate experiments have been made. None are quoted by Thomson and Thomson. It seems however that at a pressure of, say, 10 atmospheres the air molecules would be so close together that one ion sweeping round another of opposite sign would be certain to collide with air molecules, lose its angular momentum, and be captured. Under such circumstances the formula

$$\alpha = 4\pi e(w_1+w_2)$$

would be valid.

---

* *Ann. de Chim. et de Phys.* **28**, 483 (1903); *Comptes Rendus*, **137**, 177 (1903); cf. Thomson and Thomson, *loc. cit.* p. 35.

§ 4. THE COMBINATION OF SMALL IONS WITH CONDENSATION-NUCLEI CHARGED OR UNCHARGED

The significance of η_{10}. Now let us consider the circumstances in which the combinations of small ions with uncharged nuclei take place. Both ions and nuclei are subject to thermal agitation or Brownian movement, but the nuclei, being comparatively large and heavy, will be moving comparatively slowly. The frequency of collisions will depend on the sizes of the particles and on the velocities of the ions. The electrical attraction between an ion and an uncharged nucleus, being small, will not affect the frequency of collisions, but the attraction probably ensures that the ion adheres to the nucleus and so makes a large ion. We adopt as a working hypothesis the view that the expression $\eta_{10} n_1 N_0$, which by definition represents the rate of combination of small ions and neutral nuclei, also represents the frequency of collisions between such bodies.

The significance of η_{12}. In the case of collisions between small ions and nuclei which carry opposite charges the electrical attraction has to be considered as well as the Brownian movement. At a distance r from a large ion with the electronic charge $-e$ the strength of the electric field is er^{-2}. The resulting velocity of a small positive ion with mobility w_1 is accordingly $ew_1 r^{-2}$. This velocity is to be added vectorially to the random Brownian velocity.

Accordingly the number of small positive ions entering in unit time a small sphere of radius r surrounding the charged nucleus exceeds the number which would enter such a sphere surrounding an uncharged nucleus by $ew_1 r^{-2} n_1 4\pi r^2$ or $4\pi e w_1 n_1$.

More precisely it may be stated that the number of small positive ions entering in unit time the small spheres surrounding N_2 charged nuclei exceeds the number which would enter such spheres surrounding N_2 uncharged nuclei by $4\pi e w_1 n_1 N_2$. If the spheres are only just large enough to contain the nuclei it is to be expected that every small ion entering a sphere will be captured. Had the N_2 charged nuclei been uncharged the rate of capture of small ions would have been $\eta_{10} n_1 N_2$. Owing to the electrical attraction the rate is increased by $4\pi e w_1 n_1 N_2$. The total rate is, by definition, $\eta_{12} n_1 N_2$. It follows that

$$\eta_{12} = \eta_{10} + 4\pi e w_1 \qquad \text{......(4·1).}$$

Exactly the same argument leads to the analogous formula

$$\eta_{21} = \eta_{20} + 4\pi e w_2 \qquad \text{......(4·2).}$$

It was seen that the similar formula for α did not hold good, unless the molecules of the air were so close together that their distances apart were comparable with the size of a small ion. The new formulae should hold if the spacing of the air molecules is small compared with the size of a nucleus. This condition is satisfied, for at atmospheric pressure the interval between air molecules is of the order 3×10^{-7} cm., whilst the diameter of a nucleus or large ion is about 10^{-5} cm. Thus the case for the new formulae is established, at any rate so far as to encourage an appeal to experiment.

§ 5. THE VERIFICATION OF THE NEW FORMULAE

The formulae to be discussed are

$$\eta_{12} - \eta_{10} = 4\pi e w_1 \qquad \text{......(5·1)}$$

and

$$\eta_{21} - \eta_{20} = 4\pi e w_2 \qquad \text{......(5·11).}$$

Apparently the only observations available for the verification of the formulae are those made in 1925 by Nolan, Boylan and de Sachy. In their investigation they dealt with the air of a laboratory. They had facilities for measuring the rate of production of ionization, the numbers of ions, large and small, and also the number of uncharged nuclei.

Denoting by q the rate of ionization, we can write down four equations by which the combination coefficients and the observed quantities are related. The first two equations indicate that the number of small ions of one sign or the other formed in unit time is equal to the number absorbed by nuclei, charged or uncharged. The other two equations indicate that the number of uncharged nuclei receiving charges is equal to the number of charged nuclei which are neutralized. The four equations are:

$$q = \eta_{12} n_1 N_2 + \eta_{10} n_1 N_0 \qquad \text{......(5·2),}$$

$$q = \eta_{21} n_2 N_1 + \eta_{20} n_2 N_0 \qquad \text{......(5·21),}$$

$$\eta_{10} n_1 N_0 = \eta_{21} n_2 N_1 \qquad \text{......(5·3),}$$

$$\eta_{20} n_2 N_0 = \eta_{12} n_1 N_2 \qquad \text{......(5·31).}$$

The equations imply that nuclei are so much more numerous than small ions, that a small ion is sure to terminate its career by an encounter with a nucleus; the recombination of small ions with each other is ignored. It is also assumed that the combination of small ions with gross particles of dust, particles much larger but much less numerous than condensation nuclei, can be neglected. At first glance it might be supposed that, if n_1, n_2, N_0, N_1 and N_2 were all known as well as q, the four combination coefficients could be deduced. This is not the case however, for the equations are not independent.

In 1925 Nolan, Boylan and de Sachy* measured in the laboratory N_1 and n_2. The value of q was found at the same time, three separate pieces of apparatus being used. It was assumed that $N_1 = N_2$, that $n_1 = n_2$ and also that $\eta_{21} = \eta_{12}$. These assumptions imply that $\eta_{10} = \eta_{20}$.

The ranges observed were for N_1 from 3300 to 11880 ions per cm.^{3}; for n_2 from 105 to 497 ions per cm.^{3}; for q from 17·8 to 64·7 ions per cm.^{3} per second. By using the equation

$$q = 2\eta_{21} n_2 N_1,$$

it was deduced that η_{21} ranged from $6{\cdot}2 \times 10^{-6}$ to $13{\cdot}1 \times 10^{-6}$ and the average value of η_{21} was given by

$$\eta_{21} = 9{\cdot}7 \times 10^{-6}.$$

---

* *Proc. R. Irish Acad.* A 37 (1925).

From observations of the ratio N_0/N_1 the average value 1·28 was deduced and hence it was found that

$$\eta_{20} = \eta_{21}/1{\cdot}28 = 7{\cdot}6 \times 10^{-6}.$$

According to the assumptions mentioned above it followed that

$$\eta_{12} = \eta_{21} = 9{\cdot}7 \times 10^{-6}$$

and

$$\eta_{10} = \eta_{20} = 7{\cdot}6 \times 10^{-6}.$$

In 1927 Nolan and de Sachy introduced an amendment*. They gave new values of η_{12} and η_{10} whilst keeping the original values of η_{21} and η_{20}. The amendment was based on the observational result, $n_1/n_2 = 1{\cdot}11$. The equality of N_1 and N_2 was still accepted and a new assumption was made, viz.

$$\eta_{21} : \eta_{20} = \eta_{12} : \eta_{10}.$$

The amended results were

$$\eta_{21} = 9{\cdot}7 \times 10^{-6}, \quad \eta_{20} = 7{\cdot}6 \times 10^{-6},$$
$$\eta_{12} = 8{\cdot}7 \times 10^{-6}, \quad \eta_{10} = 6{\cdot}8 \times 10^{-6}.$$

These figures have to be compared with those representing the mobilities. For indoor air Nolan and de Sachy found† mobilities 1·19 and 1·38, reckoned in cm./sec. for a gradient of 1 volt/cm. Hence, using electrostatic units, we have

$$4\pi e w_1 = 4\pi \times 4{\cdot}77 \times 10^{-10} \times 300 \times 1{\cdot}19 = 2{\cdot}14 \times 10^{-6},$$
$$4\pi e w_2 = 4\pi \times 4{\cdot}77 \times 10^{-10} \times 300 \times 1{\cdot}38 = 2{\cdot}48 \times 10^{-6}.$$

The formulae under discussion require

$$\eta_{12} - \eta_{10} = 4\pi e w_1, \quad \text{i.e.} \quad 1{\cdot}9 \times 10^{-6} = 2{\cdot}14 \times 10^{-6},$$

and

$$\eta_{21} - \eta_{20} = 4\pi e w_2, \quad \text{i.e.} \quad 2{\cdot}1 \times 10^{-6} = 2{\cdot}48 \times 10^{-6}.$$

The approximate verification is satisfactory, but confirmation by additional observations is clearly desirable.

§ 6. INDIRECT ESTIMATES OF COMBINATION COEFFICIENTS AND OF q

If we assume the new formulae we can use observations of w_1, w_2, n_1, n_2, N_1, N_2 and N_0 to determine not only the η's but also q. The equations of equilibrium are

$$\eta_{10} n_1 N_0 = (\eta_{20} + 4\pi e w_2)\, n_2 N_1 \qquad \text{......(6·1)},$$
$$\eta_{20} n_2 N_0 = (\eta_{10} + 4\pi e w_1)\, n_1 N_2 \qquad \text{......(6·11)}.$$

From these it follows that

$$\eta_{10} = \frac{4\pi e N_1 (w_1 n_1 N_2 + w_2 n_2 N_0)}{n_1 (N_0^2 - N_1 N_2)} \qquad \text{......(6·2)},$$

$$\eta_{20} = \frac{4\pi e N_2 (w_2 n_2 N_1 + w_1 n_1 N_0)}{n_2 (N_0^2 - N_1 N_2)} \qquad \text{......(6·21)},$$

and we deduce that

$$q = \frac{4\pi e N_0 \left[n_1 w_1 N_2 (N_1 + N_0) + n_2 w_2 N_1 (N_2 + N_0)\right]}{N_0^2 - N_1 N_2} \qquad \text{......(6·3)}.$$

---

* *Proc. R. Irish Acad.* A 37, 71 (1927).

† *Loc. cit.* p. 83.

Let us accept the following data from the Dublin experiments:

$$4\pi e w_1 = 2{\cdot}14 \times 10^{-6}, \quad 4\pi e w_2 = 2{\cdot}48 \times 10^{-6}, \quad N_0 = 1{\cdot}28\, N_1 = 1{\cdot}28\, N_2 \text{ and}$$
$$n_1 = 1{\cdot}11\, n_2.$$

On substitution we find that

$$\eta_{21} = 11{\cdot}2 \times 10^{-6},\ \eta_{12} = 9{\cdot}9 \times 10^{-6},\quad \eta_{20} = 8{\cdot}7 \times 10^{-6},\quad \eta_{10} = 7{\cdot}8 \times 10^{-6}.$$

These coefficients, which agree well enough with those given by Nolan and his collaborators, have been determined, it will be noticed, without using absolute values of the N's and n's.

The method can be used most readily for finding q under such circumstances that the whole conductivity of the air may be regarded as due to the small ions and that the net charge on the large ions is zero. Then

$$\lambda_1 = n_1 e w_1,\ \lambda_2 = n_2 e w_2,\ N_1 = N_2$$

and $$q = 4\pi (\lambda_1 + \lambda_2)\, N_0 N_1/(N_0 - N_1) = 4\pi (\lambda_1 + \lambda_2)\, N_0 (N - N_0)/(3N_0 - N) \qquad \text{......(6·31).}$$

The difficult counts of large ions are obviated and q can be estimated for the open air by the use of comparatively simple apparatus*.

It is clear however that the method suffers from two disadvantages. In the first place the formula for q is a bad one because, in the determination of a difference like $(3N_0 - N)$, a lower order of accuracy is attained than in the measurements of N_0 and of N. Secondly there is a more fundamental difficulty. In discussions of this subject it is customary to assume that there is local equilibrium between the process of generation of ions and the processes of combination. The turbulent motion of the air, carrying ions from level to level, is ignored, as well as the conductivity current. A complete analysis would be very difficult, but in the absence of that analysis it must be anticipated that our simple formula for determining q will not always lead to consistent results.

§7. THE NUMBERS OF CHARGED AND UNCHARGED NUCLEI AND THE RATE OF DISSIPATION OF SMALL IONS.

Let the rate of dissipation of small ions of positive sign be denoted by $\beta_1 n_1$. β_1
Small ions disappear on account of combination with small ions of opposite sign or on account of combination with nuclei, charged or uncharged, so that

$$\beta_1 n_1 = \alpha n_1 n_2 + \eta_{10} n_1 N_0 + \eta_{12} n_1 N_2 \qquad \text{......(7·1).}$$

---

* An instrument designed for measurements of N and N_0, a modification of the Aitken nucleus-counter, was described in 1931 by J. Scholz, *Z. f. Instrumentkunde*, **51**, 505 (1931), but the inventor has demonstrated recently that the elimination of the charged nuclei in the receiver is very slow. The method of use which he recommends now suffers from the drawback that the mobility of the large ions has to be given an assumed constant value, *Met. Z.* **49**, 388 (1932). At Kew Observatory a separate condenser attached to a "portable" Aitken counter is being used for eliminating the large ions and is giving consistent readings.

In the foregoing discussion it has been assumed that the first term on the right of this equation is negligible in comparison with the other two, so that

$$\beta_1 = \eta_{10} N_0 + \eta_{12} N_2 \qquad \text{......(7·11).}$$

If the formula (2·3) is valid, then

$$\beta_1 = \eta_{10}(N_0 + N_2) + 4\pi e w_1 N_2 \qquad \text{......(7·12).}$$

For the sake of simplicity let us discuss the case in which there is complete symmetry as between positive and negative charges. In this case the condition for the steady state may be written

$$\frac{N_0}{1+x} = \frac{N_1}{x} = \frac{N_2}{x} = \frac{N}{1+3x} \qquad \text{......(7·2),}$$

x where $x = \eta_{10}/4\pi e w_1$ ......(7·3).

Hence it follows that

$$\beta_1 = 4\pi e w_1 \frac{2x(1+x)}{1+3x} N \qquad \text{......(7·4).}$$

It is convenient to write $\beta_1 = 4\pi e w_1 y N$ ......(7·5),

y so that $y = 2x(1+x)/(1+3x)$ ......(7·51).

This relation between x and y is illustrated by figure 1. The variables x and y are proportional to the coefficients which are used to express the rates of combination of small ions with uncharged nuclei and with nuclei of unknown character respectively. It will be noticed that, when the combination coefficients are small,

$$y = 2x \text{ approximately.}$$

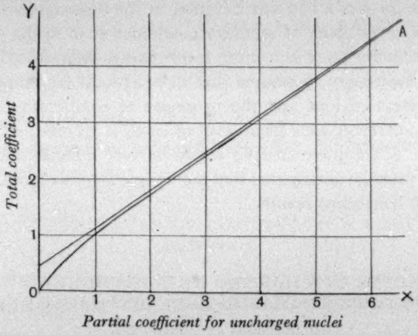


Figure 1. The total combination coefficient for small ions and nuclei as a function of the combination coefficient for small ions and uncharged nuclei.

$$x = \frac{\eta_{10}}{4\pi e w_1}, \quad y = \frac{\beta}{4\pi e w_1 N}.$$

The functional relation $y = \dfrac{2x(1+x)}{(1+3x)}$

is represented by the curve OA. The asymptote is $y = \frac{2}{3}x + \frac{4}{9}$.

When the coefficients are large,

$$y = \tfrac{2}{3}\,(x + \tfrac{2}{3}).$$

When the coefficients are small there is a superabundance of uncharged nuclei, but when the coefficients are large the numbers of uncharged nuclei and of large ions of either sign tend to equality. The limiting values of N/N_0 or $(1 + 3x)/(1 + x)$ are 1 and 3.

For comparison with observations we note that J. J. and P. J. Nolan found* in country air value of N/N_0 varying between 1·1 and 3, the mean ratio being 1·9. The value of N_0/N_1 corresponding with this mean is 2·2. The Nolans quote the following values found by other observers for N_0/N_1, 2·4 (Gockel) and 2·2 (Hess), both in the open air, 1·3 (Nolan, Boylan and de Sachy) for the air of a closed room. Accepting the formula (7·2), we deduce that for country air, with $N_0/N_1 = 2{\cdot}2$,

$$\eta_{10} = 0{\cdot}83 \times 4\pi e w_1,\quad \eta_{12} = 1{\cdot}83 \times 4\pi e w_1,\quad \beta = 0{\cdot}87 \times 4\pi e w_1 N,$$

whilst for the air of a closed room in Dublin, with $N_0/N_1 = 1{\cdot}3$,

$$\eta_{10} = 3{\cdot}3 \times 4\pi e w_1,\quad \eta_{12} = 4{\cdot}3 \times 4\pi e w_1,\quad \beta = 2{\cdot}6 \times 4\pi e w_1 N.$$

These last results are equivalent to those deduced above on p. 372 from the same observations.

It is clear that the η's and β are by no means invariable.

§8. EXCURSUS ON THE DETERMINATION OF THE DISSIPATION COEFFICIENT BY SCHWEIDLER'S SECOND METHOD.

Simultaneous observations of the dissipation coefficient and of the number of nuclei have been made by P. J. Nolan and C. O'Brolchain. In this research a method due to Schweidler and known as Schweidler's second method† was adopted. It is necessary to consider the theory of this method, for Schweidler's analysis appears to be wrong in one detail so that the rate of dissipation computed by his formula is twice as great as it should be. That the rate so computed is double that found by Schweidler's first method was demonstrated experimentally by O'Brolchain, but the origin of the discrepancy has apparently been overlooked.

The "second method" is quite simple in principle. One electrode of a closed condenser is connected to an electrometer, which is initially earthed, the other electrode is maintained at a fixed potential, and the current flowing into the former electrode is measured. Let v and C be the volume and capacity of the ionization chamber, V the potential difference and i the current. In accordance with our general notation q is the rate of production of small ions per unit volume, n_1 is the number of small positive ions per unit volume, whilst β_1 is the dissipation coefficient and w_1 the mobility. Let F be the strength of the electric field at a point on the surface S of the electrode, where the surface density of the charge is σ. Then $F = 4\pi\sigma$ and the total charge on the electrode is CV. Accordingly the current flowing into the electrode is such that

v, C
V, i
F
S, σ

$$\frac{i}{e} = w_1 n_1 \int F dS = 4\pi w_1 n_1 \int \sigma dS = 4\pi w_1 n_1 CV \qquad \text{......(8·1).}$$

---

* *Proc. R. Irish Acad.* 40 A (1931) 33.

† *Wiener Berichte* **133**, 23 (1924).

Further, in the steady state all the small positive ions which are produced either are dissipated or flow to the negative electrode. Accordingly

$$qv = \beta n_1 v + i/e \qquad \text{......(8·2)}.$$

From these equations it follows that

$$qve/i = 1 + \beta v/4\pi w_1 CV \qquad \text{......(8·3)},$$

or

$$i + Hi/V = qve \qquad \text{......(8·31)},$$

H where

$$H = \beta v/4\pi w_1 C \qquad \text{......(8·4)},$$

and H is independent of v.

In successive experiments V is varied and it is found that there is a linear relation between the values of i and i/V; so H is readily determined and the value of β can be deduced from that of H.

In this argument it is assumed that the number of small ions is the same when averaged through the volume and when averaged through a thin layer in contact with the electrode. The justification for this assumption is that the air is more or less stirred up by convection currents, and the electric current carrying the ions towards the electrode is weak. Schweidler, on the other hand, ignored the diffusion of ions and regarded the current through the ionization vessel as carried by the transfer of ions of both signs under the influence of the electric field. Thus, according to his assumptions,

$$i = (w_1 n + w_2 n_2)\, e \,.\, 4\pi CV.$$

Regarding n_1 and n_2 as equal, he gave a formula equivalent to

$$\beta = 4\pi\,(w_1 + w_2)\, CH/v$$

with $w_1 + w_2$ instead of our w_1.

O'Brolchain's experiments* may be regarded as demonstrating that our way of regarding the matter is the right one. In these experiments O'Brolchain determined β by both of Schweidler's methods. In the "first method"† the ionization chamber is allowed to stand for a considerable time with no applied voltage and the number of small ions in the final state is found by sweeping them up, by applying a strong voltage for a short time. Denoting this number by $v\,(n_1)_0$ we have the equation

$$q = \beta\,(n_1)_0 \qquad \text{......(8·5)}.$$

In the second part of the experiment a considerable steady voltage is applied and the saturation current is determined. Writing $(i)_\infty$ for the strength of this current, we have the relation,

$$qve = (i)_\infty \qquad \text{......(8·51)}.$$

Accordingly

$$\beta = (i)_\infty/ve\,(n_1)_0 \qquad \text{......(8·6)}.$$

O'Brolchain found that the value of β determined in this way was about half of that derived from the formula

$$\beta = 4\pi\,(w_1 + w_2)\, CH/v.$$

Since w_1 and w_2 are nearly equal his observations serve to verify our formula (8·4)

$$\beta = 4\pi\,(w_1)\, CH/v.$$

---

* *Gerlands Beiträge*, **29**, 1 (1931).

† *Wiener Berichte*, **127**, 953 (1918).

In criticism of the analysis by which this formula was reached it may be said that the assumption of uniform distribution is inconsistent with the fact that the ions are being urged by the electric field towards one electrode or the other. Obviously the assumption is only an approximation to the truth, but as experiments demonstrate that the relation between i and i/v is linear it is likely that the approximation is a good one. The way in which the linear relation would break down under other assumptions may be illustrated by an example.

Let us suppose that the small ions are stratified but that the large ions are so nearly uniformly distributed that the variations of β are negligible. For simplicity let us take the case of a chamber in which the electrodes are parallel planes, so large that the edge effects may be ignored. Let the distance between the planes be h, and the area A, so that $v = hA$ and $C = A/4\pi h$. Let n_1 be the density of the positive ions at a distance z from the negative electrode. Let F be the electric force, which is uniform, the effects of the space charge being negligible. The density of the current carried by the positive ions is $n_1 e w_1 F$ and therefore

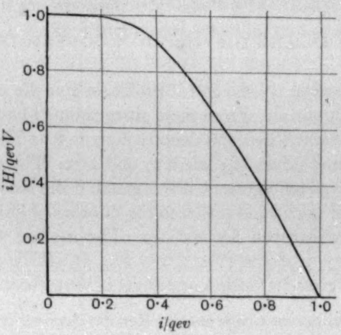


Figure 2. A hypothetical curve representing the relation between apparent conductivity and current, allowance being made for the stratification of small ions.

$$q = \beta n_1 - \frac{\partial}{\partial z}(n_1 w_1 F) \qquad \ldots\ldots(8\cdot7).$$

Subject to the condition that $n_1 = 0$ at the positive electrode ($z = h$), the solution of this equation is

$$n_1 = (q/\beta)\,[1 - e^{-\kappa(h-z)}],$$

where

$$\kappa = \beta/w_1 F.$$

The value of n_1 close to the negative electrode ($z = 0$) is given by

$$n_1 = (q/\beta)\,[1 - e^{-\kappa h}].$$

Hence it follows that the current i is such that

$$i = (qevV/H)\,[1 - e^{-H/V}] \qquad \ldots\ldots(8\cdot8),$$

where

$$H = \beta v/4\pi C w_1.$$

The relation between i and i/V is represented by the curve in figure 2 instead of by a straight line. Greater elaboration of the theory would probably lead to curves of the same type. The linear relation found by observation implies that the conditions are really simple. By that criterion our original assumption is justified.

For the purpose of the present paper it is convenient to regard observations by Schweidler's "second method" as giving the value of $\beta/4\pi w_1 e$ and the essential formula is

$$\frac{\beta}{4\pi w_1 e} = \frac{HC}{ve}. \qquad \text{......(8·9).}$$

For the Dublin experiments C/ve was $7{\cdot}18 \times 10^5$ in electrostatic units. The formula appropriate for use when H is expressed in volts is

$$\beta/4\pi w_1 e = 2{\cdot}39 \times 10^3\, H. \qquad \text{......(8·91).}$$

§9. VARIATIONS IN THE DISSIPATION COEFFICIENT FOR SMALL IONS

The Dublin Observations. Nolan and O'Brolchain give the results* of 31 observations of N and H in Dublin air. From these observations I have deduced the values of $\beta/4\pi w_1 e$ and of the ratio $\beta/4\pi w_1 eN$, denoted by y in § 7. The results are set out† in table 1. The extreme values of y are 0·27 and 1·32. The corresponding values of x being 0·175 and 1·48 (cf. figure 1), it is implied, if the theory is correct, that the ratio of the number of uncharged nuclei to the number of charged nuclei of either sign, $(1 + x)/x$, varied between 6·7 and 1·7. The median value of y was 0·74, corresponding with $x = 0{\cdot}68$ and $(1 + x)/x = 2{\cdot}5$. It will be noticed that this last estimate is nearly that given by Gockel, and quoted above, for the ratio N_0/N_1.

Table 1. *The Dissipation Coefficient β.* Results derived from observations made by "Schweidler's second method" by Nolan and O'Brolchain.

N $10^3 \times$	H	$\beta/4\pi e w_1$ $10^3 \times$	y or $\beta/4\pi e w_1 N$	N $10^3 \times$	H	$\beta/4\pi e w_1$ $10^3 \times$	y	N $10^3 \times$	H	$\beta/4\pi e w_1$ $10^3 \times$	y
53·4	20·0	47·8	0·90	25·7	10·0	23·9	0·93	21·5	4·0	9·6	0·45
40·0	4·5	10·7	0·27	25·7	7·0	16·7	0·65	21·2	11·7	28·0	1·32
36·5	12·3	29·4	0·80	25·0	6·9	16·5	0·66	21·2	9·0	21·5	1·01
36·3	13·5	32·2	0·89	24·5	6·2	14·8	0·60	21·2	8·2	19·6	0·92
35·5	8·4	20·0	0·56	23·8	7·3	17·4	0·73	20·9	6·9	16·5	0·79
34·0	9·1	21·8	0·64	23·6	5·5	13·1	0·56	20·9	9·4	22·5	1·08
34·0	6·0	14·3	0·42	23·6	6·8	16·3	0·69	20·0	7·7	18·4	0·92
32·2	6·1	14·6	0·45	22·0	9·2	22·0	1·00	17·8	5·5	13·1	0·74
29·8	7·9	18·9	0·63	22·0	9·4	22·5	1·02	17·5	6·2	14·8	0·85
29·0	6·0	14·3	0·49	22·0	10·0	23·9	1·09	17·0	6·1	14·6	0·86
29·0	8·5	20·3	0·70	—	—	—	—	—	—	—	—

The individual values of y are apparently not correlated in any way with the values of N. The assumption that the combination coefficients are invariable would evidently be far from the truth. It is to be expected that large ions with different histories will vary in size, and that the likelihood of collision between large and small ions, depending as it must on the size of these particles, will also vary.

---

* *Proc. R. Irish Acad.* **38** A, 40 (1929).

† The entries under N are to be multiplied by 1000 to give the number of nuclei per cm³

With such an idea in mind P. J. Nolan kept air in the ionization chamber for several days and followed the changes in the number of nuclei and in the dissipation coefficient. The values of N and H which he obtained* have been copied in table 2.

It will be seen that in each series of observations the number of nuclei diminished. The coefficient y, which is proportional to the combination coefficient for small ions and nuclei, increased. As Nolan points out, this coefficient varies roughly as $N^{-\frac{1}{2}}$. The combination coefficient η_{10} for small ions and uncharged nuclei, which is proportional to the x of table 2, is found, with about the same accuracy, to vary as $N^{-\frac{2}{3}}$, the product $xN^{\frac{2}{3}}$, given in the last column of the table, being approximately constant in each experiment.

Table 2. P. J. Nolan's experiments illustrating the change of the dissipation coefficient in air kept in a closed vessel for two or three days.

Dates 1928	N $10^3 \times$	H	$\beta/4\pi e w_1$ $10^3 \times$	y or $\beta/4\pi e w_1 N$	x or $\eta_{10}/4\pi e w_1$	$xN^{\frac{2}{3}}$. $10^2 \times$
April 17–20	22·0	5·5	13·1	0·6	0·5	3·9
	2·94	2·0	4·8	1·6	1·9	3·9
	1·50	1·6	3·8	2·5	3·2	4·2
	1·13	1·05	2·5	2·2	2·7	2·9
Dec. 18–19	5·25	4·8	11·5	2·2	2·7	8·1
	3·27	3·7	8·8	2·7	3·4	7·5
	1·22	2·1	5·0	4·1	5·5	6·3
Dec. 19–20	18·7	7·2	17·2	0·9	0·9	6·3
	3·41	3·0	7·2	2·1	2·6	5·9
Dec. 20–21	3·47	2·4	5·7	1·6	1·9	4·4
	2·17	1·8	4·3	2·0	2·4	4·0
	1·12	1·25	3·0	2·7	3·4	3·7

If the nuclei in the ionization chamber diminished in number by combination, not by deposition on the walls of the chamber, then the masses of individual nuclei were, at any time, proportional to N^{-1} and the areas varied as $N^{-\frac{2}{3}}$. Accordingly the observations are consistent with the hypothesis that the combination coefficient for small ions and neutral nuclei is proportional to the area of the individual nucleus.

Thus the explanation of the variation in the ratio N_0/N_1 discussed in § 7 appears to be that the ions of the laboratory air were larger than those generally to be found in country air. The lesson of our table 1 is that, in Dublin at any rate, there is no correlation between the number of nuclei and their average size.

At Kew Observatory numerous simultaneous observations have been made of the conductivity of the air and of the number of Aitken nuclei. It has been disappointing to find that there is no simple law by which these data are associated. The recognition that nuclei with different origins and different histories are bound to have different combination coefficients should help us to explain the observations.

---

* *Proc. R. Irish Acad.* **38** A, 49 (1929).

§ 10. CONCLUSION

I have felt some diffidence in publishing the new formulae without waiting for further observations by which they can be tested. My excuse must be that although the needful observations are simple in principle there are likely to be practical difficulties which may not be overcome without considerable delay. I am therefore venturing to submit this paper for publication in the hope that other investigators, who may be provided already with suitable apparatus, will undertake experiments. Enough has been said to demonstrate that such experiments will help to fill up some of the large gaps in our knowledge of atmospheric electricity.

546.92 : 537.542.2 : 548.52

THE CRYSTALLINE STATE OF THIN SPLUTTERED FILMS OF PLATINUM

By Prof. G. P. THOMSON, F.R.S., NORMAN STUART, B.Sc. and C. A. MURISON, M.A.

Received December 6, 1932. *Read February* 3, 1933.

ABSTRACT. Films of platinum spluttered in various gases have been examined by the method of electron-diffraction. They often show patterns which indicate that the small crystals are oriented with one face parallel to the surface of the specimen, the crystals being otherwise at random. The width of the rings formed by diffraction shows that in many cases the crystals are very small, of the order of 5×10^{-7} cm. Some films of platinum dioxide showed crystals of the order 2×10^{-7} cm.

§ 1. INTRODUCTION

In the course of a research in collaboration with Prof. G. I. Finch and others on the catalytic properties of thin spluttered films of platinum, we have noticed certain peculiarities in the crystalline condition of some of the films which seem worthy of note. They concern the orientation of the small crystals of which these films are composed, and the size of the crystals.

The films were prepared by spluttering in a gas—argon, oxygen, nitrogen or hydrogen—at a pressure of about 0·1 to 0·5 mm. and at voltages varying from about 500 V to 3000 V in different cases. The crystalline nature of the films was investigated with an electron-diffraction camera which had previously been used by one of us to study the surface layers formed by chemical action, and also to investigate single crystals of metal*. Briefly the method consists in the use of the wave properties of the electrons to form diffraction patterns from the crystals in the surface layer of the substance to be examined, which, when that layer is polycrystalline, are strictly analogous to the Debye-Sherrer rings obtained with X-rays. With some of the specimens these rings were uniform and sharp, indicating that the crystals forming the surface layer were arranged at random, and that each contained a sufficient number of unit cells to make them act like gratings of high resolving power. In some cases, however, the rings were relatively broad. In other cases some at least of the rings showed marked variations in intensity along their circumference.

§ 2. WIDTH OF RINGS

Three principal causes contribute to the width of a diffraction ring: (1) The geometrical width of the electron beam as determined by the diaphragms which define it; (2) the inhomogeneity of the velocities of the electrons and consequent variation in wave-length; (3) the finite size of the diffracting crystals.

---

* G. P. T., *Proc. R. S.* **128**, 649 (1930); **133**, 1 (1931).

The angular breadth B due to the last cause is given by*

$$B = \frac{2\lambda}{D}\sqrt{\frac{\log_e 2}{\pi}},$$

D, λ
N, a

where D is the thickness of each minute crystal assumed cubic in shape and λ is the wave-length. If we write $D = Na$, where a is the side of unit cube of the structure ($3{\cdot}91 \times 10^{-8}$ for platinum),

$$N = 0{\cdot}94\,\lambda/aB.$$

The homogeneity of velocity depends on the constancy of the discharge; the latter was produced by a transformer feeding two condensers in parallel each of capacity 0·022 μF, the frequency was 50 ~, and the reverse current was stopped by a valve. With a current of 0·3 mA, which was about that used, the variation in voltage is thus about 450. The broadening due to this at 30,000 V for the rings usually measured is 0·07 mm. and is negligible. This conclusion is confirmed by the fact that the larger rings were as sharp as the inner ones, while the effect of inhomogeneity is proportional to the radius of the ring.

The extreme geometrical width of the electron beam was about 2·2 mm., and the rings should be broader than this owing to diffraction occurring at different distances from the photographic plate on different parts of the specimen; actually most of the rings (see below) were less than 1·2 mm. wide. The beam was limited by two circular holes, so that it was strongly concentrated towards the centre; the width to half-intensity would be about 1·0 mm., assuming uniform distribution of the electrons. It is well known however that such beams are often narrower than the geometry would suggest, owing to the curvature of the lines of force near the holes; and this must have been the case here, for rings were observed whose half-intensity width was as little as 0·6 mm. The width of the rings was measured with dividers, and since the edge was never sharp the best estimate was made of the half-intensity width by eye. Visual measurements have been shown to give good agreement with those made by means of a photometer, and in view of the large number of plates to be measured some quick method was necessary. The values found are shown in table 1.

Table 1.

Number of plates	Half-intensity width of rings (mm.)	Number of plates	Half-intensity width of rings (mm.)
3	0·7	13	1·2
5	0·8	3	1·3
12	0·9	1	1·4
39	1·0	2	1·5
9	1·1		

All these rings showed patterns undoubtedly due to ordinary platinum. It would have been rather difficult to make any certain deductions from these results in view of possible variations of the "geometric" width of the beam with the conditions of the discharge if it had not been for a fortunate accident. A number of the plates showed, in addition to the rings due to metallic platinum, other extra rings due to some substance not yet identified but probably a compound of platinum. These extra rings were always sharp even when the rings of normal platinum were not*. The measured widths were 0·8, 0·7, 0·8, 0·8, 0·6, 0·6, 0·6 mean 0·7 mm. The associated rings had widths from 0·8 to 1·2 mm. and in the case of one specimen 2·0 mm. and 2·2 mm. (on two plates). These last have not been included in the above table as the rings were so fuzzy that they could not be identified with complete certainty as due to ordinary platinum, though it is highly probable that they were. Since there is no reason to suppose that the extra rings, which depend on the specimen tested, should occur when the testing apparatus was working in any special way, we are entitled to take 0·7 ± 0·1 mm. as giving the width of the beam due to causes (1) and (2), and to attribute any extra width to cause (3). Thus we can say that the majority of the plates show broadening due to the small size of the crystals of the spluttered platinum.

---

* W. H. Bragg, *X-rays and Crystal Structure*, p. 133.

To calculate the amount of this broadening we need to know the shape of the intensity curves due to the different causes. If both were error curves the combined breadth, b, would be given by $b^2 = b_1^2 + b_2^2$, where b_1, b_2 are the breadths due to the separate causes. If both were sharply defined the *total* breadth would be $(b_1 + b_2)$ and would be sharply defined. The actual beam is certainly not sharply defined at the edges. If all the crystals had the same size, the breadth due to this cause would have a fairly definite limit, but it is more likely that there is a graduation in sizes. It is probable that the truth lies between the two extreme assumptions.

b_1, b_2

Taking the first, a ring of width 1·0 would have $\sqrt{\{(1{\cdot}0)^2 - (0{\cdot}8)^2\}}$, or 0·6 mm. due to crystal size. This corresponds, when $\lambda = 0{\cdot}6 \times 10^{-9}$ (which is an average value), to $N = \mathbf{9{\cdot}5}$ unit cubes.

On the second assumption the same ring gives a width of 1·0 − 0·8 or 0·2 mm., which gives $N = 28$.

For a width of 1·5 mm. the two methods give $N = 4{\cdot}5$ and 8·1 respectively. Thus we may say that the majority of the rings were caused by crystals with about 20 unit cubes in the side, and a few by some with only about 6.

§ 3. RINGS OF PLATINUM DIOXIDE

In addition to the patterns which can be referred to platinum itself, others occurred when the spluttering was done in oxygen at a low or moderate voltage (less than 2000). Rings were obtained which there is reason to attribute to platinum dioxide. They were often quite sharp, especially when the platinum was spluttered below 900 V, averaging under 0·9 mm. At higher voltages they became very diffuse. Two rings were much stronger than any of the others, and these alone appeared distinct in the diffuse pattern, apart from some very faint rings farther out. The width varied from 1·5 to 2·6 mm., and the mean was 2·1. This corresponds to a size

---

[*] The following are the spacings corresponding to the main rings of this pattern (unit, 10^{-8} cm.): 4·4, 3·06 (s.), 2·06 (ms.), 1·73, 1·31 and many smaller.

of about $1 \cdot 6 \times 10^{-7}$ cm. for the small crystals. With the exception of one plate having rings 1·3 mm. wide there is nothing between these very diffuse rings and the sharp rings described above. This pattern was only found when the spluttering was in oxygen. On heating to 225° C. it passed into normal platinum, not orientated.

§4. ORIENTED FILMS

Variation in intensity round the circumference of the rings implies that the small crystals were not arranged at random. Examples of these are shown in figures 2 and 3. The extent of the orientation varies very much, from the case, such as that shown in figure 3, where the rings are almost reduced to isolated spots, to other more numerous cases in which there is a hardly perceptible difference of intensity along the circumference of some of the rings. The general nature of the orientation observable is in all cases the same, namely, that a single type of crystal plane is parallel to the free surface of the blank on which the platinum has been spluttered, the orientation being at random round the normal to this surface. In such a case the ring corresponding to the orientated plane will show a maximum of intensity in a direction normal to the surface. The rings corresponding to other planes will show maxima in different directions as can be seen from the figure, in which O, the centre of the rings, is the point in which the incident rays would meet the plate, AB is the intersection of the plane of the specimen, and the dotted lines represent the intersections of the Bragg planes with the plate. The intensity-maximum at C is due to planes which are (nearly) parallel to AB. The angle ψ between the radii corresponding to the directions of maximum intensity of different rings is equal to the angle between the Bragg planes corresponding to these rings. Thus we have

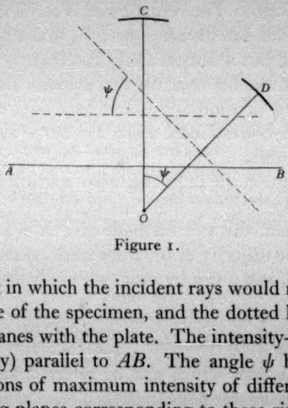


Figure 1.

ψ

$$\cos\psi = \frac{j_1 j_2 + k_1 k_2 + l_1 l_2}{\sqrt{(j_1^2 + k_1^2 + l_1^2)}\,\sqrt{(j_2^2 + k_2^2 + l_2^2)}},$$

where $(j_1 k_1 l_1)$, $(j_2 k_2 l_2)$ are the Miller indices of the Bragg planes causing the rings at C and D. Although the general nature of the orientation is always the same, the preferred plane differs in different cases. In the course of the investigation of catalytic activity 93 specimens in all were tested; of these 32 showed appreciable orientation (see table 2).

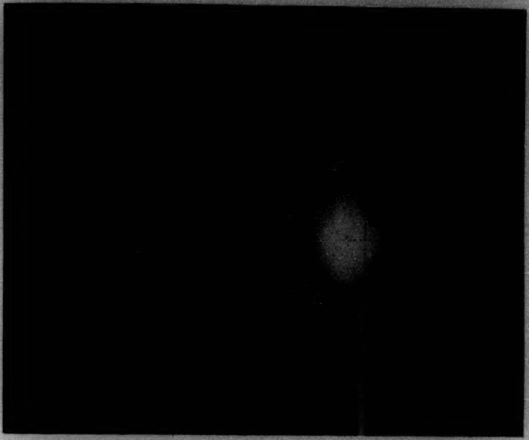


Figure 2. (100), Cubic face parallel to face of specimen.

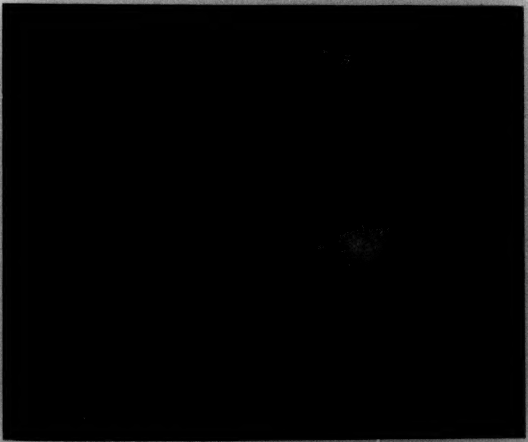


Figure 3. (111), Octahedral face parallel to face of specimen.

Tables 3 and 4 give typical measurements from some of the specimens and show agreement between the calculated and observed directions of the maxima on the various rings. The error in determining the position of the maxima depends greatly upon the extent to which the intensity is concentrated, but is seldom less than 2° or 3°, so that the agreement is as good as can be expected.

Table 2.

Number of plates	Number of specimens		Face parallel to blank surface
16	4 7 2	On quartz On glass On molybdenum	(100), cube
11	3 5 3	On quartz On glass On molybdenum	(111), octahedral
5	3 1	On glass On molybdenum	(110)
5	2	On glass	(100) and (420)
5	2	1 on glass 1 on quartz	(111) and (110) with (100) and (331) in one case

Table 3. *Plate of November* 9, 1931. Cube face parallel to surface.

(*hjk*)	± ϕ observed	± ϕ calculated
(111)	C. 60° (too black to measure exactly)	54·7°
(200)	0°	0°
(220)	45°	45°
(311)	25°, 70°	25·2°, 72·5°
(222)	60°	54·7°
(400)	0°	0°
(331)	C. 50°	46·5°, 76·7°
(420)	C. 30°	26·6°, 63·4°
(511)	C. 20°	15·8°, 78·9°

Table 4. *Plate of July* 19, 1932. Octahedral face parallel to surface.

(*hjk*)	± ϕ observed (mean)	± ϕ calculated
(111)	0°, 68°	0°, 70·5°
(200)	52°	54·7°
(220)	37°	35·3°
(311)	30°, 60°	29·5°, 58·5°
(222)	0°	0°
(331)	22°	22·0°, 48·5°
(420)	40°	39·2°

§ 5. DISCUSSION OF RESULTS

It is probable that the orientation, when it occurs, is a thermal effect produced during or after the deposition of the platinum. As the main object of the research was an investigation of the catalytic properties of the films, with which their orientation shows no connection, no special attempt was made to investigate the temperature conditions, but it was noticeable that the films which showed orientation were usually those which had been prepared at high voltages and current, and for which the cathode had been visibly hot. It is probable that the orientation occurs best over a definite range of temperature. Strong orientations occurred in two or three cases in which the cathode was at a white heat, but in one case when the cathode was dazzlingly bright no orientation was observed.

The blanks used were of three materials, molybdenum, quartz and glass. The quartz and glass blanks were cleaned in fresh aqua regia for some time before use, rinsed with distilled water, and dried on clean filter paper. The molybdenum was polished with Bluebell polish rinsed in alcohol, and rubbed on cotton wool. There was no correlation observable between the nature of the blank and the orientation, either in the frequency in which the orientation occurred or in the preferred plane. This is shown in table 2. It is doubtful if the nature of the gas has any marked effect on the types of orientation, all of which have been found with argon, and though the oxygen films show only the octahedral type and the nitrogen only the cubic type it is doubtful if much weight should be assigned to these differences, as voltage and pressure conditions were such that comparatively few of the films showed orientation at all. When several photographs were taken from one specimen the orientation shown was always the same, so that the state of the film is fairly uniform over the surface of the specimen, which was usually about 1 cm. × 1 cm. It should be emphasized that what we have here is not the formation of a film consisting of a single crystal as found in the early experiments of one of the authors* and investigated recently by Trillat and Hirsch†. Our films are analogous to those studied by Kirchner‡, who however does not appear to have found more than one kind of orientation for each of the substances which he tested.

The diffraction patterns from a single crystal, as one of us has shown§, are of quite a different character. A very interesting question, and one which the present research does not answer, is—what determines the face which takes up the preferred position parallel to the surface of the blank? If it were a question of pure chance we should expect that, since the cubic and octahedral faces are both common, the usual type of pattern would be a mixture of the two, but in fact this is very rare if it ever occurs. It appears as if some feature in the conditions determines the face. The most obvious is the temperature, but for the reason stated we have no evidence on this point. It would be a matter of great interest to investigate further in this

* G. P. T., *Proc. R. S.* **117**, 600 (1928).

† *J. de Phys.* **111**, 1932, p. 185.

‡ *Z. f. Phys.* **76**, 576 (1932).

§ G. P. T., *Proc. R. S.* **133**, 1 (1931).

direction, and the present results are offered merely as an indication of what may be expected. Their value lies in the number of specimens which have been tested and the wide range of conditions, which have resulted in a variety of patterns being found. They represent a by-product from another research and are in no sense exhaustive.

The relation of the ring pattern to the catalytic activity of the film, which was the main object of the research, will be discussed in a forthcoming paper with Prof. G. I. Finch and others, but it may be remarked here that the size of the crystals appears to have no connection with the activity, which depends on the nature of the film.

§ 6. ACKNOWLEDGMENTS

In conclusion, one of us (N. S.) would like to take this opportunity of thanking the Salters' Institute of Industrial Chemistry for the award of a Fellowship, during the tenure of which part of this research was pursued. Our thanks are also due to Mr T. Riches for his assistance in the manipulation of the apparatus.

DISCUSSION

Prof. E. V. Appleton. I wondered, on looking at the diagram of the apparatus, why a cold-cathode discharge was used in preference to a thermionic source with high vacuum conditions. The presence of gas may make it easier to get a well defined electron beam, as in modern cathode-ray oscillographs, but is it not possible that the presence of gas at the same time affected the surface of the specimen?

Dr M. C. Johnson. As the size of the particles in the surface films proved to be so small, whereas cathode-sputtered material has previously been expected to be of larger colloidal dimensions, would the authors give any detail of the method of deposition adopted to secure such small crystals? It is known that films deposited from a stream of separated atoms of metallic vapour can consist of minute crystals, which grow by the surface migration of adsorbed atoms. Have the crystals described in this paper grown similarly, or is their final size determined by their size as multi-atomic aggregates before striking the surface? If the cathode particles are as large as they have generally been supposed to be, and yet form deposits whose individual particles are smaller than those which grow after being deposited from purely atomic streams, the structure of the surface film seems independent of all history before impact and may depend on the temperature and smoothness of the target above.

Prof. G. I. Finch. As regards § 3, in the course of recent experiments Mr A. G. Quarrell and I have found that the definition of the diffraction rings due to cathodically sputtered platinum dioxide, and hence the crystal-size, depends in the main upon, and decreases with, the rate of deposition. We have observed a similar effect with both sputtered and evaporated metal films, provided the receiver was cool.

Heating the receiver usually brought about a growth of the crystal-size in the deposited film and frequently resulted in orientation. Thus it does not seem that the crystal-size can be properly ascribed to the discharge characteristics, except in so far as these may afford a measure of the rate of deposition. At the end of § 5 the view is expressed that the size of the crystals appears to have no connection with the (catalytic) activity. Messrs Coles, Quarrell and I have, however, recently carried out further experiments, the results of which strongly suggest that crystal-size and activity are in fact intimately associated with each other. In collaboration with Dr Hodge* and Dr Thompson† I have shown that metals are sputtered as atoms.

With regard to Prof. Appleton's question concerning the cold cathode, Mr Quarrell and I prefer this type of discharge tube for the range of accelerating voltages we require (15–80 kV.) on account of its simplicity and the avoidance of light-fogging of the photographic plate. In conjunction with the cold cathode we also employ a diode which acts as a current-limiting device. It will be readily seen that the combination of a cold-cathode discharge tube supplied through a saturated diode combines the advantages of both the cold and hot-cathode types of discharge tubes without their disadvantages, and renders simple the attainment of a perfectly steady accelerating voltage.

AUTHORS' reply. In reply to Prof. Appleton: The gas-filled tube is on the whole easier to control than the hot-filament tube. We have never observed any effect of gas on the specimen, possibly because the impact of the cathode rays cleans the surface, though effects have of course been observed with slow electrons.

In reply to Dr M. C. Johnson: The experimental conditions of deposition were not intentionally designed to produce films with any particular crystal-size. Sputtering was carried out with a platinum wire cathode of length 5·5 cm. and diameter about 0·75 mm. The films were usually deposited on to either glass or quartz-plate receivers, optically flat and polished. Molybdenum and silver blocks, also polished, were used at one time and gave the same results. Films sputtered in oxygen at the lowest possible discharge currents and potentials were found to give very sharp diffraction patterns of oxide. At high currents of the order of 10 mA. and potential of the order of 1800 V., very diffuse patterns were obtained. These results might be explained by analogy with the connection between crystal-size and rate of growth in solution. In this case the rate of sputtering would be the controlling factor.

As Prof. Finch has said, it is now generally accepted that sputtering takes place by individual atoms, so there is nothing surprising in the final aggregates being small. Probably heat treatment, when it occurs, makes them grow larger. As regards the influence of particle-size on activity, the statement was only meant to apply to the range of size considered in this paper, and more especially to the platinum particles.

---

* *Pooc. R. S.*, A. **124**, 303 (1929).

† *Proc. R. S.*, A. **129**, 315 (1930).

551·594·11

WEEKLY MEASUREMENTS OF UPPER-ATMOSPHERIC IONIZATION

By E. V. APPLETON, F.R.S. and R. NAISMITH, A.M.I.E.E.

Received January 7, 1933. *Read February* 3, 1933

ABSTRACT. A series of weekly measurements of the maximum ionization content of the Kennelly-Heaviside region of the ionosphere is reported and discussed. The ionization is found to be 2·2 times as intense on a summer noon as on a winter noon, and, in general, slightly less in 1932 than in 1931. This reduction is considered to be probably due to the approach of sunspot minimum and, together with other evidence, suggests that the ionizing agency from the sun varies by as much as 60 per cent during the 11-year solar period. Although ultra-violet light is accepted as the major ionizing agency, thunderstorms most probably constitute one of the subsidiary causes. The possibility that thunderstorms might cause upper-atmospheric ionization has been previously suggested by C. T. R. Wilson.

§1. INTRODUCTION

In a recent paper* we have described an experimental method of estimating the maximum ionic content of the Kennelly-Heaviside region of the ionosphere. The possibility of making such a determination arises as follows. If we project vertically upwards wireless waves of gradually increasing frequency (and therefore gradually shorter wave-length) we find that for a certain critical frequency penetration of the Kennelly-Heaviside region takes place, and reflection begins from an upper region in which the ionization is usually more intense. Such penetration is therefore indicated by a discontinuity in the curve in which equivalent height is plotted as a function of electric wave frequency. From this curve the critical frequency at which the penetration of the lower region begins is found by inspection, and from this value the maximum ionization content of the region is deduced.

§2. THE RELATION BETWEEN MAXIMUM IONIZATION AND CRITICAL PENETRATION FREQUENCY

The way in which the maximum ionization is estimated when the critical penetration frequency is known has been previously discussed at length for the case in which the ionization consists of electrons and also for the case when it consists of ions of molecular mass, so that only a word or two of explanation is required here. Although the problem cannot as yet be fully dealt with in terms of a wave treatment, as opposed to a simple ray treatment, we assume that reflection at vertical incidence takes place at the level at which the refractive index is equal to zero. Thus if we find the frequency which just penetrates, say, the lower region, we assume that for frequencies just less than this the refractive index is reduced to zero at the level of maximum ionization. For this condition we have, as has previously been shown

---

* *Proc. R. S.*, A. **137**, 36 (1932).

$$N_{\max} = \frac{3\pi m}{2e^2} f^2,$$

$N_{\max}$, e, m
f

where $N_{\max}$ is the ionic (or electronic) content per cm.^{3}, e and m are the charge and mass respectively of an ion (or electron), and f is the critical penetration frequency. The relation between $N_{\max}$ and f is shown in figure 1, the broken curve referring to ions (oxygen atoms) and the continuous curve to electrons.

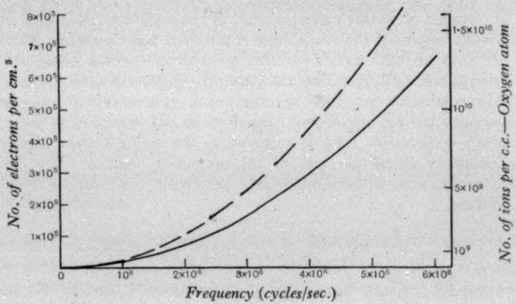


Figure 1.

In the present paper we are not concerned with the absolute values of $N_{\max}$ but only with its variation.

§ 3. WEEKLY MEASUREMENTS OF MAXIMUM IONIZATION

In our previous work the measurements of the maximum ionization in the Kennelly-Heaviside layer were made over the whole 24-hours for selected winter, spring and summer days. These measurements showed that the ionization is a maximum about noon and falls off steadily as sunset approaches. The ionization continues to fall rapidly after sunset until an almost stationary night value is reached. Before and during ground sunrise the value of $N_{\max}$ increases rapidly, and after sunrise more slowly, until the maximum noon value is again reached. We have pointed out that the general diurnal variation curves with their marked correlation with sunset and sunrise leave little doubt that the chief agency responsible for the ionization is of solar origin and travels through the earth's atmosphere in straight lines. We have also given reasons, based on the observations made by one of us during the solar eclipse of 1927, for concluding that this agency is ultra-violet light. That this view is substantially correct has been shown by the observations made by Dr J. Henderson in Canada, and by others, during the eclipse of the sun on August 31, 1932.

But in discussing our measurements of diurnal variation we pointed out that although there was a seasonal variation, the ionization at summer noon being about $2\frac{1}{2}$ times that at winter noon, we had encountered many days when the ionization appeared to be in excess of the normal seasonal value. We also recorded that on a number of nights the ionization in the lower region actually may increase at a time when any solar radiation propagated rectilinearly could not possibly be reaching the area immediately over the place of measurement.

In order to investigate the possible subsidiary ionizing agencies for *E* region we have made weekly estimates of the ionization throughout a period of nearly two years, from January 1931 to November 1932. These have all been made at the Radio Research Station, Slough, with signals from the emitting station at the National Physical Laboratory. The measurements were made every week on either Thursday or Friday round about noon.

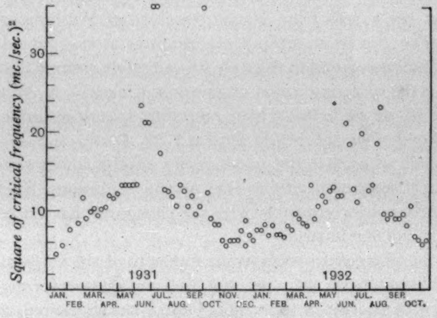


Figure 2.

In figure 2 the variation of the square of the critical frequency (which is proportional to maximum ionization content and may be translated into such values with the aid of figure 1) is shown over the whole period of observation. It will be noted that the seasonal variation is clearly marked, the ionization being more intense on a summer noon than on a winter noon. In our previous work on this subject we were led, from a comparison of the average results obtained on summer and winter days, to conclude that the summer-noon ionization was of the order of 2·9 times that on a winter noon. The more extensive data now available and shown in figure 2, however, show that abnormally high values of ionization are very frequently encountered in summer, so that if we wish to consider the undisturbed seasonal variation it is preferable not to take average values but to assess it from the general trend of the curve*. If we do this we find a somewhat lower figure for the ratio of summer to winter ionization, of the order of 2·2.

---

* We shall discuss more fully our reasons for doing this later in the paper, when we consider the possible nature of the sources of this abnormally high ionization.

If we compare the results obtained in 1931 with those obtained in 1932 we find that the general level of ionization is lower in the latter series. This is most easily seen by a comparison of the spring and autumn values. We have reasons, which we shall explain later, for excluding the summer values from such a comparison. It is not possible to give an exact figure for the average reduction from 1931 to 1932, but the diminution is probably of the order of 10 to 15 per cent. It is natural to associate this with the general fall in solar activity in the sequence of the solar cycle, since the last sunspot maximum was in 1928 and the succeeding sunspot minimum is expected in 1933–4.

If work in future years confirms this variation with the sunspot cycle, and we are able to ascribe it even only in part to the ultra-violet light from the sun, it will follow that such radiation varies with solar activity over a wider range than does the so-called solar constant.

In this connexion it is interesting to recall that L. W. Austin and I. G. Wymore* have shown that the signals from Nauen, received at Washington, are approximately 1·8 times as intense at sunspot maximum as at sunspot minimum. Since waves of 13,000 metres are used in this case we can safely assume that the Kennelly-Heaviside layer is the reflecting region in question. Using G. N. Watson's theory of the propagation of waves between two reflecting spherical surfaces, one of the authors† has shown that the result obtained by Austin and Wymore may be interpreted as indicating that the conductivity of the lower reflecting layer is 1·6 times as great at sunspot maximum as at sunspot minimum. Such a variation of ionization is clearly not incompatible with the change we have noted between the ionization in 1931 and that in 1932‡.

In such terrestrial measurements of the intensity of the sun's ultra-violet light as have been published we do not, at present, find any support for the view that such radiations vary with sunspot activity. G. Pettit§ has measured the ratio of the ultra-violet radiation transmitted by silver ($\lambda\ 0{\cdot}32\mu$) to the green light transmitted by gold ($\lambda\ 0{\cdot}5\mu$) on many days since 1924, and although the early observations seemed to indicate that this ratio varies with solar activity it is now considered that the variations observed are more probably due to changes in the atmosphere. Further work is necessary before it is possible to assess from ground measurements how much of the variation is due to terrestrial causes, such as changes in the amount of ozone, and how much is really due to changes in solar emission.

It is also of interest to compare the above measurements of critical frequency which were made in South-East England with those which we have deduced from the series of measurements of equivalent heights at different frequencies made at the Bureau of Standards, Washington, and communicated to us by Science Service, U.S.A.

---

* *Proc. Inst. Rad. Eng.* **16**, 166 (1928).

† E. V. A. *International Research Council Second Report on Solar and Terrestrial Relationships*, p. 16 (1929).

‡ Although we are inclined to interpret our results as indicating quite a substantial variation in the sun's ultra-violet light during the solar period, it should be mentioned that the fact that the variation of solar control over radio transmission during this period increases with latitude suggests that charged particles must also be taken into account.

§ *International Research Council Third Report on Solar and Terrestrial Relationships*, p. 105 (1931).

Unfortunately, measurements in Washington are made not at local noon but at a time which is two to three hours after mid-day, so that the comparison has to be made with caution. We have, however, compared our measurements of noon ionization with the American measurements of afternoon ionization, and find them to be of the same order of magnitude when corresponding periods are compared, so that we may conclude that noon ionization in Washington is on the average greater than noon ionization in England. This result is readily explained if we assume that the ionizing agency is ultra-violet light, and remember that Washington is situated in latitude 38·8° N whereas our measurements were made in latitude 51·5° N.

§4. THE CAUSES OF ABNORMAL IONIZATION

Although it is clear that the major source of daytime ionization for the lower region is ultra-violet light, evidence has been steadily accumulating which indicates that it is necessary to take other possible causes into account to explain departures of the ionization from the normal seasonal and diurnal values. Much of this evidence has accrued from observations made at night when, the level of normal ionization being low, departures from it are readily recognized. For example, in 1930 it was pointed out by one of us*, as a result of a long series of measurements of the equivalent height of *E* region, that on some occasions "either the recombination of ions is prevented or there is some ionizing agent present which can influence the dark side of the earth." The same matter was mentioned in our paper referred to above where we conclude that "there is some agency which produces nocturnal ionization beyond the ordinary amount constituting the residue from the day-time." Schafer and Goodall† and Ranzi‡ have also noted the same effects and arrived at similar conclusions. Notable interest, however, is to be attached to the work of Ranzi, since he has suggested that this source of nocturnal ionization is possibly connected with the troposphere. From a series of observations on 330 occasions Ranzi concludes that the abnormal night ionization in region *E* is associated with the presence of barometric depressions either at the point of observation or at a place to the north of it. This result is of special importance in connexion with the reasons advanced, as far back as 1924, by C. T. R. Wilson for concluding that thunderclouds contribute ionization to the atmospheric conducting layer, in the form of either intense ionization currents or lightning flashes. It is therefore of interest to test a fairly substantial set of data to see whether there is evidence that thunderstorms constitute the essential link in the correlation between barometric depressions and abnormal ionization. Our data for the period January 1931 to November 1932 were handed to Mr F. E. Lutkin for general statistical examination. He called our attention to a note which he had communicated to the Superintendent of the Radio Research Station on September 2, 1932. In this note he had reported abnormal shortening of the skipped distance for 15-mc./sec. waves which had been observed by a British wireless amateur, Mr E. R. Peach, in the thunderstorm conditions of August 18–19, 1932, and had suggested that this might indicate specially intense ionization, in the ionosphere, associated with local thunderstorms. It will be seen from figure 2 that the critical frequency on August 18 was in fact very high. In a further note dated September 12, Mr Lutkin had remarked on the high value of critical frequency, the low attenuation of 15-mc./sec. signals, and the high thunderstorm activity which had marked the preceding day, September 11.

---

* E. V. A., *Proc. R. S.*, A. **126**, 567 (1930).

† *Proc. Inst. Rad. Eng.* **20**, 1131 (1932).

‡ Ranzi, *Nature*, 130, 368 (1932).

In order to test these points further, he then compared our data with thunderstorm reports, and found such a close relation between days of high critical frequency and days of British thunderstorms that he undertook a detailed comparison of the data for the period January 1 to July 31, 1932, with a "thunderstorm index figure" derived as follows. During this period observations on the distribution of European sources of atmospherics were made at Slough for half-an-hour near 13h G.m.t. each week day. The peak amplitudes of all atmospherics recorded in this operation as coming from sources within 3000 km. were summed to form the thunderstorm index figure. The relation between ionization density in *E* region and this thunderstorm index was found to be represented by a correlation coefficient so high as 0·75. The comparison was not carried further because of the interruption of the direction-finding work after July and the relative inadequacy of sampling before January. It is, however, noteworthy that the occasions of abnormal ionization of *E* region in thunderstorm conditions on the dates in August and September already mentioned and a similar occasion on October 11 are not included in the period for which the high correlation coefficient was obtained.

In view of the above conclusion we are now inclined to attach special importance to a series of signal-intensity measurements made by Dr J. Hollingworth and one of us on signals from the station of St Assise ($\lambda = 14{,}350$ m.) received at Slough. These observations were such that it was possible to deduce the values of both ground wave and down-coming wave. One afternoon in May 1929 a thunderstorm area passed between the two stations when observations were in progress, and it was noticed that when the area reached the great circle joining the stations, atmospheric absorption became so pronounced that the reflected wave was undetectable. Although this is only an isolated case we believe it to be evidence of intense ionization at a considerable height, since the absorptive and refractive influence of ionization only become of importance when the pressure is so reduced that the time between two collisions of an ion with gas molecules is of the order of the electric wave frequency.

As we have already recorded, we have frequently found that a magnetic storm has been accompanied by abnormally high ionization in the lower region, though a correlation is by no means invariably found. We can only say that if there is a very big magnetic storm the ionization in region *E* is increased. In this connexion it is important to note that when from any cause, such as a magnetic storm or thunderstorm, *E*-region ionization is increased, there is not usually a corresponding increase in region *F*. In fact we have on some days found conditions the reverse of normal, *E*-region ionization being greater than that in *F* region. We can therefore safely conclude that the agency or agencies which cause such abnormal ionization in region *E* is not the same as the agency (i.e. ultra-violet light) which ionizes both *E* and *F* regions in the normal manner.

The known influence of solar activity in terrestrial magnetism, which is shown by recurrence tendencies connected with the solar rotation-period of 27 days, naturally suggests the examination of our maximum ionization data for such recurrence tendencies. It has already been shown by various writers that periodogram analysis of long-distance signal-intensity data show evidence of such a periodicity corresponding to solar rotation. In this connexion it should, however, be pointed out that signal intensity is often an ambiguous index of ionospheric ionization, for it is well known that increase of ionization may, owing to absorption limitation, result in a reduction of signal intensity, whereas in other cases such an increase, by the removal of electron-limitation, may cause just the reverse result. No such objection applies to ionospheric-ionization measurements for the lower region as deduced from the critical penetration frequency, so that such data are of the type most suitable for comparison with other geophysical data. But although an examination of the smooth curve drawn through the weekly values does give a slight suggestion of a recurrence tendency with a period of 27 days, we do not believe that the data are sufficiently detailed for this result to be accepted with confidence. It is quite clear that daily readings are necessary, and it is hoped that it will be possible to obtain them in the future.

§5. ACKNOWLEDGMENTS

The work described in the paper was carried out as part of the programme of the Radio Research Board of the Department of Scientific and Industrial Research. We wish to express our indebtedness to Mr R. A. Watson Watt, Superintendent of the Radio Research Station, Slough, for providing us with facilities for the measurements, for making available the data for the "thunderstorm index figure," and also for helpful discussion at various stages of the work. We also wish to thank Dr R. L. Smith-Rose for arranging for the special use of the National Physical Laboratory emitter in connexion with these experiments.

Our special debt to Mr F. E. Lutkin, of the Radio Research Station, Slough, has been mentioned in the text, while to Mr D. Brunt, of the Meteorological Office, we owe thanks for assistance in the discussion of the results.

APPENDIX

In a paper previously referred to* C. T. R. Wilson discussed the effects of thunderclouds on the rarefied regions of the upper atmosphere. Even if there were no ionized regions due to other causes, Wilson showed that the electric forces due to thunderclouds were sufficient to cause one. Also, he showed that if an ionized region already existed the electric forces between such a layer and the thundercloud would produce ionization by collision, so that discharges between the cloud and the layer would probably take place.

---

* *Discussion on ionization in the atmosphere*, Nov. 28, 1924. See *Proc. Phys. Soc.* **37**, 32 D. (1925).

It is of interest to consider in greater detail the processes pictured by Wilson, taking into account the variation of air pressure between the cloud and the layer. In doing so we shall be obliged, to some extent, to idealize the problem. We shall assume that the layer consists of highly-ionized air and plays the part of the filament in a large-scale diode, the positive head of the thundercloud acting as the corresponding anode. The actual state of affairs is shown inverted in the accompanying figure.

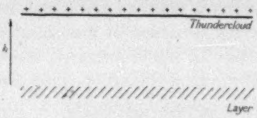


Figure 3.

i, h, σ_0 Let i be the current per unit area flowing in the direction of the height h. If σ_0
σ is the pressure of the air at the level of the layer, the pressure σ at height h is equal
H, E, ρ to $\sigma_0 e^{h/H}$, where H is of the order of 10 km. Let E be the electric force, ρ the space-
k charge density, and k the ionic mobility at any height. If we assume that the
k_0 mobility is proportional to the pressure, k is equal to $k_0/e^{h/H}$, where k_0 is the mobility of the ions at the level of the ionized layer.

From Poisson's equation we have

$$dE/dh = 4\pi\rho \qquad \text{......(1).}$$

Also the equation of current continuity may be written

$$i = k_0 e^{-h/H} \rho E \qquad \text{......(2),}$$

so that

$$\frac{dE}{dh} = \frac{4\pi i e^{h/H}}{k_0 E} \qquad \text{......(3),}$$

or

$$E^2 - E_0{}^2 = \frac{8\pi i H}{k_0}(e^{h/H} - 1) \qquad \text{......(4),}$$

E_0 where E_0 is the field at the surface of the layer. If the current is space-charge limited, $E_0{}^2$ is equal to zero, so that we have

$$E^2 = \frac{8\pi i H}{k_0}(e^{h/H} - 1) \qquad \text{......(5),}$$

as the representative space-charge equation.

To make an estimate of the vertical current we assume that the field near the thundercloud is, say, 1/10 of the sparking value, that is 10 e.s.u./cm.; we take H as 10 km. and h as 80 km. The value of k_0 is most uncertain, but if the pressure of the air at 80 km. is of the order of 0·02 mm., k_0 must be at least 10^7 e.s.u. Thus i calculated from (5) is $1{\cdot}3 \times 10^{-2}$ e.s.u. or $4{\cdot}3 \times 10^{-12}$ A./cm.^{2}

If the field increases two-fold this current is increased four times. But on the other hand the estimate is probably a high one, in view of the fact that we have considered the positive charge on the cloud to act as an infinite plane. According to Wilson's theory of the maintenance of the earth's electric charge and the air-earth current we are to regard thunderstorms as supplying positive ions to the upper layer, where they diffuse all over the globe and become the downward current in regions where there are no thunderstorms. We can, however, easily see how a thundercloud can contribute the ½ A. of current which the 2000 thunderstorms, in action at once, are required to supply in order to maintain the whole downward air-earth current of 1000 A.

It should be noted that either in the thunderstorm case or in the fine-weather case there are to be found space charges both near the ground and near the layer. It is easily shown that there is a certain height at which the space charge is a minimum. From (2) and (5) we have, eliminating E,

$$\rho = \sqrt{\left(\frac{i}{8\pi k_0 H}\right)} \cdot \frac{e^{h/H}}{\sqrt{(e^{h/H} - 1)}} \qquad \text{......(6),}$$

which expression is a minimum when $e^{h/H} = 2$, that is to say about 7 km. below the layer boundary.

It is also of interest to follow up Wilson's suggestion that the ionization current between the layer and the upper part of the cloud will be augmented by ionization by collision. This should most readily take place where the ratio of the electric force to the pressure is a maximum, that is to say, where $E/\sigma_0 e^{h/H}$ is a maximum. With the aid of (5) it is easily shown that this condition obtains at $h = 0{\cdot}7\,H$, or at a distance of 7 km. below the layer.

Let us compare the values of E/σ at this height of 7 km. and also at the top of the thundercloud where $h = 80$ km.

We have, on substitution,

$$\left(\frac{E}{\sigma}\right)_{7\text{ km.}} \Big/ \left(\frac{E}{\sigma}\right)_{80\text{ km.}} = 27.$$

In other words, when the field near the cloud is only 1/27 of the sparking value, the field at a distance of 7 km. from the layer has reached sparking value and the production of intense ionization currents takes place. This result suggests that perhaps the first effect of a thunderstorm would be to produce a subsidiary region of ionization about 7 km. or so below the Kennelly-Heaviside layer.

The electric charge required to give the increased ionization observed is considerable. The volume in question cannot be much less than 1 km.^3 and a simple calculation from the wireless data shows that the electric density must be of the order of 100 coulombs (of electrons) per km.^3 or 10^6 coulombs (of ions) per km.^3 The simple discharge of the positive head of a thundercloud into the upper layer is evidently not sufficient to produce such intense local ionization, and it is clear that the electric charges must be considerably augmented in some way by the processes of ionization by collision.

DISCUSSION

Prof. S. CHAPMAN. I am much interested in the authors' estimate of the variation of ionization in the *E* layer in the course of the sunspot-cycle; it is of the same order as the sunspot-cycle variation in amplitude of the solar diurnal variation of terrestrial magnetism. The corresponding lunar diurnal magnetic variation, on the other hand, shows a much smaller dependence on the sunspot epoch, and for long I have interpreted this as indicating that there are different ionizing agents in the two regions in which these magnetic variations arise. I hope that radio evidence bearing on this difference will in time become available.

Dr D. OWEN. It appears from the formula on which the disseminations of maximum ionization content are based that an estimate should be attainable of the thickness of the lower or *E* layer of the ionosphere. According to the interpretation given on the first page of the paper, as the critical frequency of the electric waves rises, so the reflecting stratum concerned gets higher. If, then, the time of the double journey is measured for a series of frequencies up to that required for penetration of the layer, the depth of this should be deducible. It would be interesting to know if the authors could give an estimate of the thickness obtained in this way, and of its dependence on time of day or the seasons of the year.

Mr F. E. LUTKIN. In connection with the seasonal variation in ionization of the *E* region as shown in figure 2, while at first sight the annual variation immediately drives one to attribute this to changes in the sun's zenith distance, in view of the close correlation, mentioned in the text, between the thunderstorm index figure and ionization for each day irrespective of abnormality, I would suggest that some at least of the seasonal variation may be attributed to the seasonal variation of thunderstorm activity. The fact that the mean summer (July–August) level of the thunderstorm index amounts to 3·1 of the winter (November–December) value is in itself significant. The higher ionization at Washington, referred to in the paper, might also be looked for in view of its proximity to the West Indian tropical thunderstorm belt.

AUTHORS' reply. The agreement between our estimate of the variation of ionization in region *E* over the sunspot cycle with that previously calculated by Professor Chapman for the corresponding variation in conductivity of the layer responsible for the solar diurnal magnetic variation is perhaps one further example of the gratifying way in which the results obtained by magnetic and wireless methods are converging. Curves in which equivalent height is plotted against electric wave frequency can be drawn, so that it is possible to estimate the depth of penetration as suggested by Dr Owen* but as yet no data are available which would enable one to decide whether this depth varies diurnally and seasonally. We certainly agree with Mr Lutkin that it is not improbable that thunderstorms may be contributing to the seasonal variation of ionization. But in this connection it must be remembered that during the solar eclipse in Canada on August 31, 1932, Dr J. Henderson found that the temporary withdrawal of the sun's ultra-violet light caused a 60 per cent reduction of the ionization in region *E*.

* See *Proc. Phys. Soc.* **42**, 336 (1930).

621.396.2.029.1:551.594.11

AN AUTOMATIC RECORDING METHOD FOR WIRELESS INVESTIGATIONS OF THE IONOSPHERE

By J. A. RATCLIFFE, M.A. and E. L. C. WHITE, B.A.
Cavendish Laboratory, Cambridge

Communicated by Prof. E. V. Appleton, F.R.S., January 11, 1933. *Read February* 3, 1933.

ABSTRACT. An apparatus for continuous automatic recording of the equivalent height of wireless echoes returned from the ionosphere is described. The Breit and Tuve method is employed, and both the transmitter and the time base at the receiver are synchronized with the a.c. mains. Some specimen records are reproduced and are used to illustrate the normal diurnal variation of equivalent height. Attention is directed to a common abnormal occurrence of increase of ionization in the lower or *E* region during the hours of darkness, without a corresponding increase in the upper or *F* region. Reasons are given for supposing that this may be due to the ionizing action of storm clouds, as suggested by C. T. R. Wilson.

§ 1. INTRODUCTION

DURING the last few years much information has been obtained about the electrical condition of the ionosphere* by interpreting wireless signals returned from it. The two most useful methods have been the frequency-change method of Appleton and Barnett and the echo method of Breit and Tuve. The results have generally been obtained during rather infrequent "all night runs," in which photographic records of the effective height of the deviating regions were made at intervals of ten or fifteen minutes. The results showed considerable variation from night to night and it is difficult to know what should be taken as typical of the normal night behaviour and what should be taken as abnormal. As is usually the case with geophysical phenomena, it is necessary to observe continuously and daily in order to deduce the normal behaviour. Clearly this is impossible unless an automatic recording apparatus is devised which will work without attention for long periods at a time. A short preliminary account of such an apparatus, for making automatic records of the effective height of the reflecting regions in the ionosphere, has already been given(1). The present paper is a full account of this apparatus together with a discussion of some of the more important results which have so far been obtained from the automatic records†.

---

* The term "ionosphere" has been suggested to denote the ionized regions of the upper atmosphere.

† While the work now to be described was being carried out some other preliminary reports of similar work have been published(11, 12, 13).

§2. APPARATUS

A method of continuous visual observation, which however did not give automatic records, has already been described by one of the present authors⁽²⁾. The present method is, in principle, the same as the visual method, with some important modifications required to make it yield automatic photographic records.

The Breit and Tuve echo method is employed.

A transmitter is caused to emit short wave-trains of radio-frequency at regular intervals of $\frac{1}{50}$ sec. The duration of the wave-trains, or pulses, is 10^{-4} sec. On arrival at a nearby receiver (about $1\frac{1}{2}$ km. from the transmitter) the wave-trains are amplified and rectified, and the resulting direct current pulses are applied to the vertically deflecting plates of a cathode-ray oscillograph, to the horizontal deflecting plates of which a linear time base, synchronized with the frequency of occurrence of the pulses, is applied. As a result, a stationary pattern of the form shown in figure 1

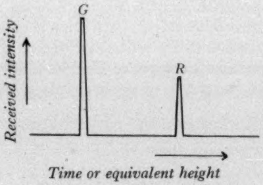


Fig. 1. Appearance of stationary pattern on oscillograph screen.
G, ground wave; *R*, reflected wave (echo).

appears on the oscillograph screen, owing to persistence of vision. The peak marked *G* corresponds to the reception of the ground wave, and occurs simultaneously with the emission of the pulse from the transmitter, the time of travel over the distance of $1\frac{1}{2}$ km. between transmitter and receiver being negligible. The peak marked *R* represents the reception of the signal after it has been returned from the ionized regions of the upper atmosphere, with a time lag of a few milliseconds. From the time lag t the equivalent height h' of the ionized region responsible for the return of the ray may be deduced from the relation $h' = \frac{1}{2}ct$, c being velocity of light in free space. The displacement of the peak *R* from the peak *G* is thus proportional to the equivalent height of the deviating region; and if we slowly draw out the pattern in a vertical direction, we shall have immediately a graphical representation of the changes of equivalent height of the deviating region with the time of day.

t, h'
c

This is accomplished by forming an image of the pattern on a strip of photographic paper which is moved at about one inch per hour in a vertical direction. The receiver is arranged to saturate for large signals, so that for all intensities of the signal greater than a certain limiting value the tips of the peaks *G* and *R* lie on the same horizontal line. An image of this line is formed on a slit covering the photographic film, figure 2.

The chief feature of the present apparatus, as distinct from that previously described, is the method of synchronization of the oscillograph time base with the transmission of the pulses. For automatic operation, when the apparatus is left to itself for as much as twelve hours at a time, this synchronization must be of a much higher order than that previously achieved by means of a flashing-neon lamp circuit.

Practically perfect synchronization has been attained by using the same a.-c. supply mains to control both the generation of the pulses and the oscillograph time base. The method of control at the transmitter and receiver will now be described.

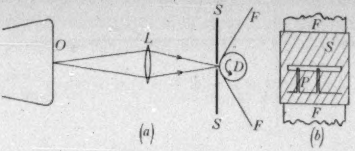


Fig. 2. Optical arrangement for photographic recording. *O*, oscillograph screen; *L*, lens; *SS*, slit; *FF*, bromide paper film, driven past *SS* by the rotating drum *D*; *P*, image of echo pattern formed by *L*.

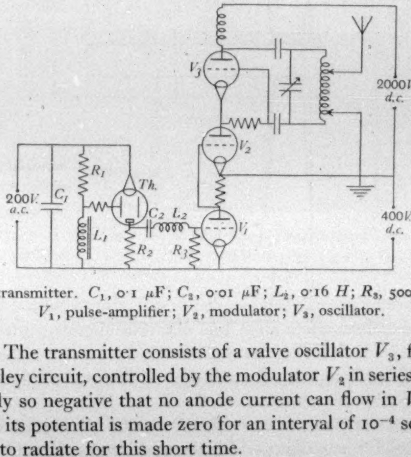


Fig. 3. Circuit of transmitter. C_1, 0·1 μF; C_2, 0·01 μF; L_2, 0·16 H; R_3, 5000 Ω; *Th*, thyratron; V_1, pulse-amplifier; V_2, modulator; V_3, oscillator.

Transmitter. The transmitter consists of a valve oscillator V_3, figure 3, arranged in a simple Hartley circuit, controlled by the modulator V_2 in series with it. The grid of V_2 is normally so negative that no anode current can flow in V_2 and V_3, but at $\frac{1}{50}$-sec. intervals its potential is made zero for an interval of 10^{-4} sec., thus allowing the transmitter to radiate for this short time.

The required short unidirectional pulses on the grid of V_2 are generated by the thyratron *Th* and its associated circuit. The potentials of the anode and grid of the thyratron are varied at the frequency of the a.c. supply but the potential of the grid is caused to lag about 90° behind that of the anode by means of the inductance L_1 and resistance R_1, so that the arc strikes when the anode potential is near its maximum value. When striking occurs, almost the whole of this potential is suddenly thrown across R_2, and excites free oscillations in the circuit $C_2 L_2 R_3$ (completed by *Th* and C_1). The constants are so chosen that the first half oscillation occupies about 10^{-4} sec., and the damping, combined with the excessive negative bias on V_2, is sufficient to prevent the further oscillations from having any effect, figure 4. The half oscillation is amplified by V_1 and applied to the grid of V_2.

The length of the pulses can be altered to suit any purpose by adjustment of the constants C_2, L_2, R_3 whereas the frequency of occurrence is determined by that of the a.c. mains (50 per sec.).

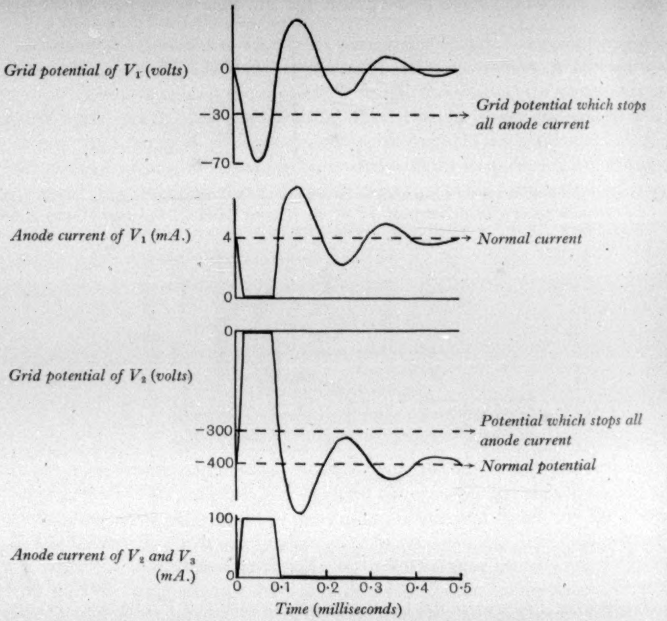


Fig. 4. Production of short pulse from heavily damped oscillation in circuit C_2, L_2, R_3, figure 3.

All filaments in the transmitter are fed from the a.c. supply and the two h.t. supplies are derived from rectifiers. Also, the grid bias for V_2 is obtained, in effect, from the h.t. for V_1, so that the whole apparatus runs entirely off the a.c. mains. As it contains no mechanical moving parts it requires no attention whatever, and has often been left running for three or four days continuously. Its starting and stopping may easily be controlled automatically by a time switch.

The transmitting aerial consists of a half-wave horizontal aerial supported at a height of 45 ft., and fed by a single-wire transmission line, adjusted as described by Everitt and Byrne(3).

Receiver. The signals are received on a loop aerial, or a horizontal aerial, to which reaction is applied by an entirely independent valve. This considerably increases the sensitivity without introducing valve "noise." A screen-grid valve in conjunction with a local oscillator is used to convert the signal to a frequency of 110 kc./sec., at which it is amplified by a three-stage resistance-capacity-coupled screen-grid intermediate-frequency amplifier, with band-pass filters for the input and output. The damping and coupling in the filters is arranged to give sensibly uniform amplification for frequencies from 100–120 kc./sec. The output filter feeds a push-pull grid detector stage V_7 and V_8, figure 5. The advantages of this system are that it responds to very high modulation frequencies, and gives no appreciable amount of intermediate-frequency current in the anode circuit.

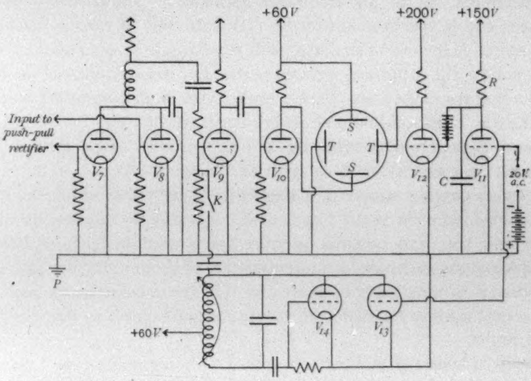


Fig. 5. Circuit diagram of time base and of final stages of receiver. V_7, V_8, Push-Pull rectifier; V_9, V_{10}, L.F. Amplifiers; V_{11}, *R*, *C*, Time-base generating circuit; V_{12}, Time-base amplifier; V_{13}, Calibration-oscillation synchronizer; V_{14}, Calibration-oscillation generator.

The rectified output has the form of short unidirectional pulses similar to those used for modulating the transmitter, and after amplification by two resistance coupled low frequency stages V_9 and V_{10} it is applied to the vertically deflecting plates *S*, *S* of the oscillograph. The pulses arriving at the grid of V_{10} are negative, so that if the h.-t. supply for this valve is limited to about 60 volts or less a small echo suffices to reduce the anode current to zero and produce the maximum deflection, and any increase of intensity cannot increase the deflection. This is the "saturation device" mentioned above.

Synchronized time base. The synchronized linear time base is provided by a battery of 150 volts charging a $0{\cdot}1$-μF condenser *C* through a $0{\cdot}5$-Ω resistance *R*, figure 5. While it is rising through the first 15 volts the potential across the condenser is practically proportional to the time, and this potential is amplified by V_{12} and applied to the plates *T*, *T* of the oscillograph controlling the horizontal deflection. The condenser *C* is arranged to be rapidly discharged by the valve V_{11} once during each cycle of the a.c. supply, which is the same supply as that controlling the thyratron at the transmitter. This discharge takes place during part of the positive half-cycle of the a.c. supply to the grid of V_{11}. During the rest of the cycle this grid is so negative that no anode current can flow, negative grid bias being supplied by the battery, so that the rate of charging of C is unaffected by the presence of the valve V_{11}. The time scale can be made as open as desired by suitably altering C and R. When it is made very open the spot traverses the oscillograph screen in a small fraction of a cycle and remains at the end of its trace for the remainder of the cycle, owing to flow of grid current which occurs in V_{11} as soon as the potential across C is equal to the potential of the bias battery; eventually C is again discharged by V_{11}. The time base is calibrated, both for uniformity and for absolute rate of movement, by the low-frequency oscillator V_{14} which has a frequency of 750 per sec., and is synchronized to the 15th harmonic of the a.c. by V_{13}, so that when the switch K is closed a stationary sine wave would be seen on the oscillograph if it were not for the saturating device (i.e. the low anode-potential on V_{10}) which flattens the positive half-cycles. Thus a broken line is photographed on to the film through the slit. These calibration lines are automatically registered on the films for a few seconds at each hour, serving also as timing marks. The period of the broken line is $\frac{1}{750}$ sec., corresponding to an equivalent height of $\frac{1}{2}c\,.\,\frac{1}{750}$ or 200 km.

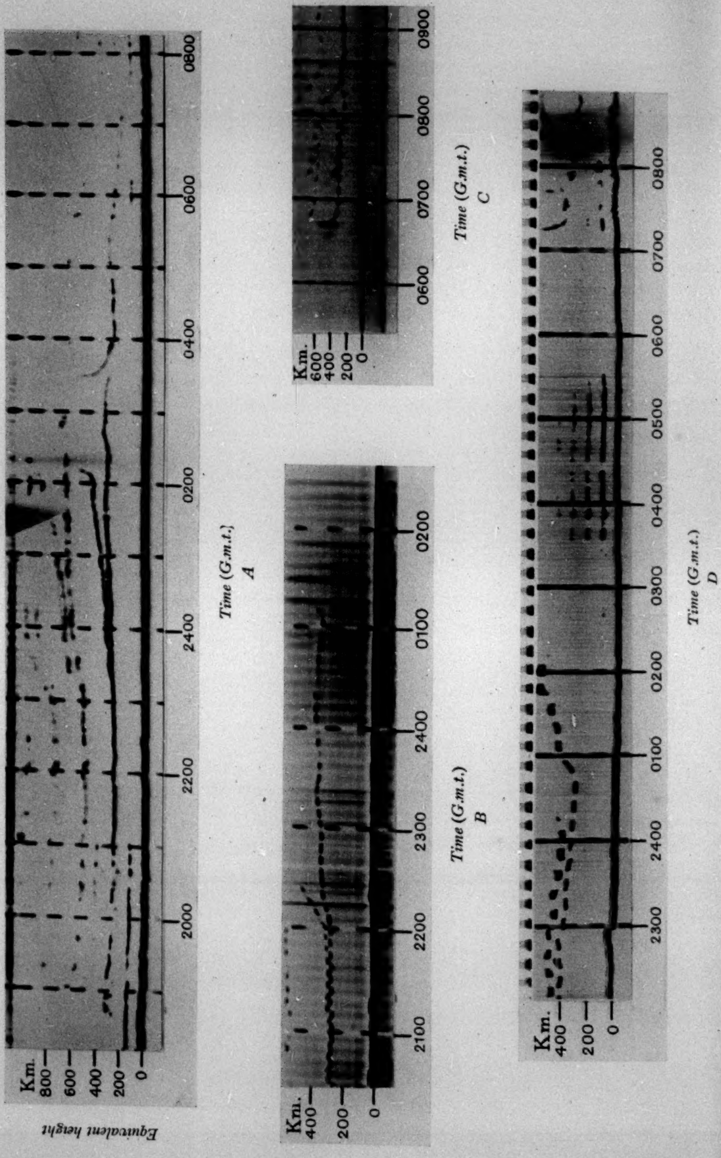
The camera consists simply of a revolving drum round which the film passes immediately behind a slit about 1 mm. wide. An ordinary achromatic camera lens of focal length 5 in. and nominal aperture $f/6$ is used to form an image of the oscillograph pattern on the slit, at a magnification of about unity (see figure 2 above). The film used is 59-mm. paper bromide film. The drum is driven through reduction gears, by a synchronous a.c. motor, to ensure constant speed, so that the film speed is about 1 in./hr.

A Cossor cathode-ray oscillograph with a "photographic-type" screen is employed, and with only 400 volts on the anode it is found to give ample intensity. Under these working conditions the life of the tube, even when run continuously, is found to be very satisfactory.

§3. DISCUSSION OF RECORDS OBTAINED

Normal behaviour. The main object of taking automatic records of the kind described here is to discover what is the normal type of variation of the equivalent height with time of day, and how this variation alters throughout the year. It is also possible that the occurrence of days showing a departure from the normal type may be correlated with the occurrence of other geophysical phenomena, such as magnetic storms. At present the apparatus has not been operating for a sufficient time for yearly variations to be investigated or for extended correlations with other phenomena to be attempted. Sufficient records have been obtained, however, to indicate clearly what is to be considered as normal behaviour, and to point to a very common type of abnormal behaviour.

The plate shows some typical records obtained with the apparatus here described. *A* in the plate is a reproduction of a night-time record obtained on 1st–2nd June 1932 on a wave-length of 100 m. It starts at 1800 G.m.t. and finishes at 0830 G.m.t. The



A, 100 m. June 1/2, 1932; *B*, 75 m. July 25/26, 1932; *C*, 75 m. October 11/12, 1932; *D*, 150 m. December 14/15, 1932.

hours are marked by the vertical calibration lines. These lines also serve as a calibration for effective height. The distance between the ends of two successive dashes in a line corresponds to an effective height of 200 km., as is indicated at the side of the record.

This record gives an example of what we have found to be the normal summer-time behaviour on this wave-length. During the day reflection takes place from the *E* region at an equivalent height of about 120 km. This is seen on the record between 1810 and 2100 hours. Multiple reflections from this region give marks on the record corresponding to equivalent heights which are integral multiples of 120 km. (e.g. between 1850 and 2100 hours). At about 1830 hours reflection from an effective height of about 260 km. becomes apparent (*F* region). An overlap between the *E* and *F* regions usually occurs; if it appears to be absent a stronger transmitter would probably show it up. Finally the *E* reflection vanishes completely and we are left with the *F* reflection alone. The time of this final transfer from *E* to *F* is 2100 hours.

Whenever the *E* region is recorded its height is nearly 125 km.; the extreme limits recorded over two months' observations on this wave-length are 114 and 138 km. This indicates the existence of a sharply defined layer at this height. The effective height does not increase appreciably before the *E* region gives place to the *F* region. On records obtained with this wave-length there is no doubt about the discontinuity of the jump from the *E* to the *F* region. It is always recorded as a discontinuity as shown in *A* in the plate, and has never been recorded as a gradual increase of height. This is important in view of doubts which have recently been cast on the two-layer hypothesis of the ionosphere[*].

When reflection from the *F* region is properly established the effective height of the region rises gradually to about 280 km., and then the echo splits into two components having different effective heights, as shown at 2330 hours. The uppermost of these (F'') then rises rapidly to about 500 km. and finally disappears at about 0210 hours. In the record of the plate the other component (F') of the split echo remains throughout the night. This occurs only under suitable conditions of wave-length and ionization. A more usual behaviour is for the lower component to rise rapidly to an effective height of about 500 km. and then to disappear an hour or two later than the upper component. This behaviour is shown in record *B* in which F'' ceases to be reflected at 2220 and F' ceases to be reflected at 0110[†].

There is next an interval during which no reflection takes place. About 30 minutes before sunrise, reflection of F' once more begins, at first at a great effective height (500 km.), but the effective height decreases rapidly. About an hour afterwards F'' appears and decreases in height to coalesce with F'. In *C* in the plate the drop of F' is seen at 0645 and that of F'' at 0715. In this record F'' appears to rise again and come down finally at 0815. In *A* in the plate the drop of F'' occurs at

---

[*] It is, however, noticeable that, with records obtained recently on a wave-length of 175 m., there are distinct signs of a gradual change in effective height from the *F* region to the *E* region near sunrise.

[†] In *B*, *C* and *D* in the plate the dotted nature of the records is due to the fact that a special polarized receiver was used, which was switched so as to receive only F' or F''. The dashed line at the top of the record is made by an indicating device. An account of this receiver will be published elsewhere; for the purposes of the present paper the broken lines should be imagined to be completed.

0330 hours. An hour or two after sunrise, which here occurred at 0350, the effective height of the F region has dropped to about 260 km., and the E region at 125 km. begins to appear, and remains throughout the day.

The most interesting feature of this normal daily behaviour is the splitting of the echo from the F region. This behaviour is similar to that previously described by Appleton and Builder$^{(4)}$ and ascribed by them to the effect of the steady magnetic field of the earth. It is supposed that, during the night, the electron-density in the F region decreases until it is no longer sufficient to reduce the refractive index to zero for one of the elliptically polarized waves, which may be propagated, according to the magneto-ionic theory, so that this wave will cease to be reflected (disappearance of F''). There will still be enough electrons, however, to reflect the other elliptically polarized wave F', and the recombination has to proceed for about another hour before this in turn ceases to be reflected.

It may be shown that the refractive indices μ_0 and μ_e become zero for the two waves for the following values of critical electron density N.

$$\mu_0 = 0 \text{ when } N = \frac{3}{2}\frac{mp^2}{4\pi e^2} = N_0$$

$$\mu_e = 0 \text{ when } N = \frac{3}{2}\frac{mp^2}{4\pi e^2}\left\{1 - \frac{p_1}{p}\right\} = N_e.$$

N_0, μ_e, N_e Here μ_0 and N_0 refer to the ordinary wave, and μ_e and N_e to the extraordinary wave,

m, e m, e are mass and charge of electron,

p $p =$ the angular frequency of the wave, and

p_1, H $p_1 = He/mc$ where H is the earth's field in gauss.

t The time interval t, between the vanishing of F'' and F' therefore gives us the time which must elapse for the maximum electron-density in the ionosphere to change from N_0 to N_e. If this decrease is due to the recombination of positive and negative ions with a recombination coefficient α it may be shown that

$$\frac{1}{N_e} - \frac{1}{N_0} = \alpha t.$$

Thus from the observed time t taken from the records it is possible to calculate α. The results so far obtained show that the time interval t is somewhat variable. The variability may be due to the fact that the maximum of ionization does not occur at the same height from night to night, so that the pressure and hence the recombination coefficient is different on different nights, or it may be due to the fact that, even during the night, some hitherto unknown cause of ionization is present*. The order of magnitude of this variation is from 20 min. to 3 hr. and the mean time is about 1 hr. for a wave-length of 100 m. This gives $\alpha = 1{\cdot}5 \times 10^{-9}$. In view of the uncertainty of our knowledge of the atmospheric pressure at these heights and of the magnitude of the recombination coefficient at low pressures, a comparison of this value with the theoretically predicted value would not seem to serve any useful purpose.

---

* It may be that effects of this kind are correlated with the abnormal behaviour described on the next page.

However, this value agrees fairly well with that of 9×10^{-9} found by Eckersley by quite a different method*.

An interesting feature of the splitting phenomenon is the very great effective height which the two echoes attain before they ultimately vanish. In interpreting this phenomenon it must be remembered that the effective height depends on the group velocity of the waves. In the presence of a steady magnetic field the group velocity is related in a complicated way to the phase velocity, but it can be shown that even in the general case the group velocity is approximately equal to the reciprocal of the phase velocity. At the highest point of the trajectory, where the ionization-density reaches the critical value, the phase velocity is very great and the group velocity is therefore very small. The total time of travel of the group is therefore determined, to a large extent, by the geometrical distance over which the electron density is nearly critical. When the wave is just on the point of penetrating the F region entirely, reflection takes from a point where N is a maximum and the ionization-gradient is gradual. A considerable length of the geometrical path is then traversed with the ionization-density nearly critical and with the group velocity abnormally small, so that the total time is considerably lengthened. When there are more than enough electrons to reflect the wave, reflection takes place from a point where the gradient of ionization is sharper and only a short length of the geometrical path lies in the region of critical ionic density, and hence of small group velocity, so that the group retardation effect is less noticeable. There must, of course, be an increase of geometrical path in going from the place where the ionization is not critical to the place where it is critical; but this increase is probably much smaller than the apparent increase due to the low group velocity. The present experimental method does not enable this increase in geometrical height to be determined.

Abnormal behaviour. It has been pointed out above that on most records for these wave-lengths the E-region echo disappears and gives way to the F-region echo round about sunset, and appears again round about sunrise. This we call the "normal" behaviour. On several occasions, however, it has been observed that after the E echo has disappeared in the usual way near sunset, it has reappeared for a few hours round about midnight†. It has then disappeared again and reappeared at sunrise in the normal way. In the typical cases there is always an interval between the disappearance of the normal E echo at sunset and the appearance of the abnormal echo. It appears that this must imply an increase in the E-region ionization during the midnight hours. This cannot be due to any ionizing influence which is propagated rectilinearly from the sun, for sunset at a height of 100 km. occurs 40 min. after ground sunset. Now from the correlation between sunrise and the incidence of the normal E echo in the early morning, it is fairly certain that the normal E-region ionization is produced by something which is propagated rectilinearly from the sun, either ultra-violet light or uncharged corpuscles. There thus appears to be reason for supposing that the abnormal *E* ionization and the normal *E* ionization are due to different causes. This supposition receives support in another way from our records. The incidence of the normal *E* region at sunrise is always closely correlated with an increase of the ionization of the *F* region. This is shown, for example, in the record *A* in the plate in which the appearance of the *E* region is preceded by a joining together of the two components of the split *F* echo and by a marked decrease in the effective height of the *F* echo as a whole. It looks as though the ionization of both the *F* region and the normal *E* region is increased simultaneously by an ionizing agent propagated rectilinearly from the sun. It is quite different, however, with the abnormal *E* region, as it appears from some of the records that the increase of ionization which is responsible for the appearance of this region is not accompanied by a corresponding increase of ionization in the *F* region. Thus in *D* in the plate reflection of the *F* echoes ceased at 2415 and 0205 and began again at 0715 and 0745 in the ordinary way. It seems fairly certain that between 0205 and 0715 there were not enough electrons in the *F* region to produce reflections. It is, however, found that between 0330 and 0530 reflection took place from the *E* region with such intensity that four reflections were recorded, and this without any reappearance of the *F* region echo. The *E* region had therefore been ionized to a density sufficient to give an echo, without any apparent increase in the *F*-region ionization. There seem to be two possible explanations of this occurrence. Either the abnormal *E* region is ionized by some influence which comes from outside the atmosphere and is capable of passing through the *F* region without ionizing it, or the ionization is produced by some source situated below the *E* region, so that its influence will be felt by the *E* region more strongly than by the *F* region. If the first of these alternatives is supposed correct it must further be supposed that the ionizing agent is not propagated rectilinearly from the sun. A stream of charged particles coming from the sun and deviated by the earth's magnetic field so as to reach the dark side of the earth is a possible source of ionization of this kind. Such a stream would produce the most intense ionization near the end of its range, and so might ionize the *E* region without ionizing the *F* region. It has been supposed that the ionization due to such a stream is responsible for magnetic storms, and so it seems reasonable to look for a correlation between magnetic storms and the occurrence of the midnight *E* region. Over the limited period during which the apparatus has been running it has not been possible to find any such correlation.

---

* Although, for comparison with Eckersley's value, we have here calculated the recombination coefficient α, it is by no means certain that the electrons are lost by recombination; they may be rendered ineffective by attachment to neutral molecules.

† Similar observations have been recorded by Appleton and Naismith(6), Schafer and Goodall(7), and Ranzi(8).

When we discussed with Prof. C. T. R. Wilson the second possibility, a terrestrial source of ionization, he pointed out to us that such a source was probably available in thunder clouds and shower clouds. In a discussion at the Physical Society(5) on ionization in the atmosphere he stated that "if there were no already existing conducting layer there is little doubt that a thunder-cloud would itself cause ionization in the upper atmosphere." He discussed two possible mechanisms by which the thunder cloud or shower cloud might produce ionization in the ionosphere. (1) The electric field due to the electric moment of the cloud may itself produce ionization at heights above 80 km. where the pressure is sufficiently low; and (2) by its accelerating action on charged particles the electric field of a thunder cloud may produce very penetrating corpuscular radiation, which in turn may produce ionization in the ionosphere. It appears that clouds of this type may provide just such a terrestrial source of ionization as our experiments seem to indicate. In looking for a correlation between the occurrence of the abnormal *E* region and thunder clouds or shower clouds it is important to remember the following points stressed by Prof. Wilson. "The vertical electric force at a point (at a height of 60 km.) may not be due solely to a thunder cloud vertically below it; all thunder clouds within a considerable area will contribute to it." "It is possible that the electrical field of a large rain cloud, which would not be regarded as a thunder cloud, may be strong enough to cause discharge in the atmosphere above it."

The suggestion that storm clouds may be responsible for ionizing the lower region during the hours of darkness receives further support from Ranzi's observation(9) that the appearance of the "abnormal *E* region" is correlated with the occurrence of meteorological low pressure conditions. Our results entirely confirm his observations and seem to show an even closer correlation with thunderstorms and heavy rainfall. The observed fact that the associated storm centres may be some distance removed from the place of observation, suggests the possibility that the extra ionization produced by the storm may spread by diffusion in the *E* region.

It is of special interest to notice that the echo from the abnormal *E* region in the night is much less absorbed than that from the normal *E* region in the daytime, as is evidenced by the large number of multiply reflected echoes which are received at night with sufficient intensity to be recorded. In spite of this, however, both types of reflection occur at approximately the same height. The explanation of these facts may be along two different lines; either the difference in absorption is due mainly to a change in the temperature of the ionosphere between day and night (the absorption depending on the collisional frequency and hence on the temperature), or the temperature remains roughly constant and the ionization-distribution changes, so that there is less ionization in the night-time in an absorbing region situated beneath the deviating region. The latter type of explanation would agree with a suggestion previously made, on quite different evidence, by Appleton and Ratcliffe(10).

§4. ACKNOWLEDGMENTS

We wish to express our thanks to Prof. C. T. R. Wilson for the many helpful discussions we have had with him, and for the characteristic readiness with which he has always put his deep knowledge of thunderstorms at our disposal. We also wish to thank Mr L. B. Turner for providing us with an ideal situation for the erection of our transmitter in the Cambridge University Engineering Laboratory.

REFERENCES

(1) E. L. C. White. *Nature*, **129**, 579 (1932).
(2) E. L. C. White. *Proc. Camb. Phil. Soc.* **27**, 445 (1931).
(3) W. L. Everitt and J. F. Byrne. *Proc. Inst. Rad. Eng.* **17**, 1840 (1929).
(4) E. V. Appleton and G. Builder. *Proc. R. S.*, A, **44**, 76 (1932).
(5) C. T. R. Wilson. *Proc. Phys. Soc.* **37**, 32 D (1925).
(6) E. V. Appleton and R. Naismith. *Proc. R. S.*, A, **137**, 36 (1932).
(7) J. P. Schafer and W. M. Goodall. *Proc. Inst. Rad. Eng.* **20**, 1137 (1932).
(8) and (9) I. Ranzi. *Nature*, **130**, 368 (1932).
(10) E. V. Appleton and J. A. Ratcliffe. *Proc. R. S.*, A, **128**, 133 (1930).
(11) T. R. Gilliland and G. W. Kenrick. *Proc. Inst. Rad. Eng.* **20**, 540 (1932).
(12) H. Rukop and P. Wolf. *Z. f. Tech. Phys.* **3**, 132 (1932).
(13) I. Ranzi. *Nuovo Cimento*, **8**, 258 (1931).

DISCUSSION

Mr R. Naismith. The rather sudden appearance of triple echoes from the *E* region, shown as *D* in the plate, suggests a very rapid increase in ionization. I should like to ask the authors whether they consider that the electric field due to the electric moment of a cloud and its accelerating action on charged particles could, under comparatively normal conditions (i.e. with no well-marked storm centre within a considerable area of the observing site) in these latitudes at midwinter produce such a sudden increase in the ionization of *E* region. It is perhaps unfortunate that the record chosen to illustrate the appearance of abnormal *E* echoes was taken on December 14–15, 1932. On that particular occasion the largest magnetic disturbance of recent months took place, which strongly suggests that the abnormal ionization in *E* on this occasion was due to increased magnetic activity. It will be appreciated that the time of sunset (quoted at the foot of page 407) at a height of 100 km. will vary with the declination of the sun.

Mr F. E. Lutkin. Mr Naismith has expressed doubts whether the record of abnormal night ionization in *E* layer, shown in record *D* for December 14, 1932, should be associated in midwinter with thunderstorm activity, and I must confess to surprise at finding a similar abnormality in *E* during the extensive anticyclonic conditions of January 25. Ranzi states that the majority of his cases of midnight *E* are associated with a depression at or to the north of his Italian station, and the authors express agreement with his findings. May I, therefore, suggest a mechanism which will hold good for Ranzi's general condition and also for the winter cases quoted above. A depression to the north of Italy is associated with a meteorological front, a region of sharp temperature-contrast, where warm moist air is being forced up over cold air extending out over the Mediterranean. Because the area is over sea, associated electrical phenomena will probably occur chiefly during the night hours. Similar low-pressure areas to the north or north-west of the British station will have similar fronts extending over the near Atlantic. Although no marked depression lay over the north of England on either of the dates referred to above, extensive frontal systems existed in the north Atlantic, and since the frequency of thunderstorms over sea areas varies very little with season there would be equal probability of finding night E from this cause all the year round, and doubts in connexion with the winter season disappear. I therefore suggest the possibility that midnight E indicates an electrically active front over the sea within some 1000 km. of the recording station. Whether the longitudinal distance of the front from the station bears any relationship to the hour at which E is recorded might be worthy of investigation.

Dr M. TAYLOR. The very elegant recording method described in the paper is likely to prove extremely valuable in wireless investigations of the ionosphere. On the theoretical side I think it would be very helpful if the authors would indicate the principles on which their theoretical discussion of group velocity is based. Prof. Appleton has discussed the meaning of group velocity in an ionized medium without the complications of two refractive indices introduced by an external magnetic field, and we are accustomed to the independence of the ordinary and extraordinary waves in a doubly refracting crystal in which the two refractive indices are constant. But in a medium of varying ionization under the action of an external magnetic field the refractive indices change continuously, and the ordinary and extraordinary waves, when they reach a place of different ionization, will each split up and produce an ordinary and extraordinary wave with refractive indices corresponding to the new ionization-density. Thus the ordinary and extraordinary waves cannot, without further investigation, be regarded as pursuing independent paths, as they may in a doubly refracting crystal, and this resplitting complicates the meaning of group velocity in the ionosphere. Hitherto I have looked upon the experimental results regarding split echoes of long delay, which the authors describe, as giving empirical evidence as to the nature of group velocity, which awaited theoretical explanation, rather than as experimental confirmations of properties of the medium predicted by theory. It would be very interesting if the authors could tell us shortly how to show that "the group velocity is approximately equal to the reciprocal of the phase velocity."

Dr D. OWEN. I think the Society is to be congratulated on the succession of interesting papers on the ionosphere recently presented by several workers in this field. The progress made in the technique of measurement is indeed remarkable, and has been duly followed by a stream of very interesting information.

As to the effect of thunderstorms on the ionization of the E layer, is it considered possible that there is an actual transference of ions, from a layer 10 km. from the earth to the E layer at, say, 100 km.? If so a considerable time-lag would seem to be required, and may perhaps have been observed.

Authors' reply. It does not seem to us that the sudden appearance of an echo from the E region necessarily implies a *rapid* increase of ionization, as suggested by Mr Naismith; the appearance of the multiple echoes simultaneously probably indicates merely an absence of absorption, as is mentioned in our last paragraph. The time given for sunset at 100 km. is only meant to be a rough value. We are aware of the effect of the sun's declination, and are obtaining some interesting results in this connexion by recording the time of commencement of the F echo throughout the year.

With reference to the remarks of several speakers as to the possible mechanisms of ionization of the abnormal E region, it will be clear from the paper that at present we are only suggesting possibilities, and a complete discussion must be postponed until further data are available. If, however, the phenomenon is to be ascribed to occurrences in the lower atmosphere, it seems reasonable to suppose that rain-cloud action of the type suggested by C. T. R. Wilson is the chief mechanism, and that any state of affairs which leads to the production of this type of cloud may be correlated with the phenomenon. In particular, if meteorological fronts prove to be correlated with the effects we have described, it must be in virtue of the fact that the appropriate type of cloud occurs in the frontal region. We are well aware of the importance of such fronts, and are engaged in exploring their connexion with our phenomenon; Ranzi himself* drew attention to their effect on wireless signals.

We are aware that the record of December 14–15 coincided with an intense magnetic disturbance as well as with an extremely deep meteorological depression, and so far as this record alone is concerned either of our explanations may be the correct one.

Dr Taylor's remarks raise two points in which we have been specially interested. The first is that a single pulse sent into the ionosphere is often returned as two discrete pulses and not as a single broadened pulse such as might be expected from the "splitting and resplitting" argument which she outlines. Although we consider that there are theoretical reasons for expecting this behaviour when the properties of the medium change slowly with distance, it is sufficient to take it, from the point of view of this paper, as an experimental fact as she suggests. It then seems necessary to suppose that the original group is propagated, at each point in the medium, as two independent groups. This brings us to the second point: "What is the group velocity in a magneto-ionic medium with constant ionic density?" In a uniform medium of this kind the ordinary conception of
μ' group velocity holds, and the group refractive index μ' is given in terms of the
μ phase refractive index μ by the usual expression

$$\begin{aligned}\mu' &= \mu + p\frac{d\mu}{dp}\\ &= \frac{1}{\mu}\left\{\mu^2 + \tfrac{1}{2}p\frac{d}{dp}(\mu^2)\right\},\end{aligned}$$

p where p is the angular frequency of the wave. In the absence of the magnetic field the factor in the bracket is unity and $\mu' = \mu^{-1}$. In the presence of the magnetic field the magnitude of the factor can be estimated under any given conditions by sketching the curve of μ^2 against N for the frequencies p, $p + \Delta p$ and $p - \Delta p$ and performing the differentiation numerically. We have developed simple rules for sketching the curves of μ^2 against N, and using these we find, for the wavelengths here considered, that the factor is of the order unity except near $\mu = 0$, and then it becomes large. Near $\mu = 0$, however, the factor μ^{-1} itself becomes considerably larger and dominates the expression, so that, to a first approximation, we may take μ' equal to μ^{-1} for all values of μ; and in particular μ' is very large when μ is small, which is the deduction used in the paper.

---

* *Nuovo Cimento*, 8, 98 (1931).

In reply to Dr Owen: we have not yet sufficient data to decide which of the mechanisms suggested by Prof. C. T. R. Wilson is most important in the ionization of the ionosphere by storm clouds. It seems fairly certain that an actual transference of ions from the cloud to the E region is not so important as the production of ionization in, or near, the E region by the field of the cloud or by penetrating radiation produced by the cloud.

536.212.3:677.6

THE TRANSMISSION OF HEAT THROUGH FABRICS*

By M. C. MARSH, M.A., Ph.D., F.Inst.P., Wool Industries Research Association, Leeds

Communicated by Dr S. G. Barker, December 9, 1932. *Read Febraury* 17, 1933

ABSTRACT. The results obtained in earlier papers$^{(1, 2)}$ have been analyzed to determine the effects of air permeability and of perforations on the thermal insulating properties of fabrics. It is subsequently shown that there is a heat-interchange between the convection currents and the fabric which is important in considering the flow of heat through such insulators.

§ 1. INTRODUCTION

A large number of thermal insulators, such as textile fabrics, are permeable to air and allow the transmission of radiant heat through their interstices. Such insulators generally have not a smooth surface, due to the interlacing of the constituent yarn, and thus the measurement of surface temperatures as ordinarily understood is not possible. Because of their compressible nature, their power of thermal transmission is changed by such compression as would occur during testing in the usual type of thermal-conductivity apparatus.

The thermal insulating properties of fabrics have been studied by the author$^{(1, 2)}$ by means of an apparatus involving two horizontal concentric cylinders maintained at different constant temperatures, in which the sample of fabric under test was supported as freely as possible in the resulting annular space in the form of an intermediate concentric cylinder. Guard rings eliminated end effects, and due experimental precautions were taken.

The following were the dimensions of the apparatus. In every case a length of 25·0 cm. is used. The diameter of the hot inner cylinder is 5·50 cm. giving an area of 431 cm^2. The outer boundary is 12·70 cm. in diameter internally and, unless otherwise stated, is considered as blackened.

The results obtained for a very wide range of fabrics were expressed in terms of *thermal insulating value* (T.I.V.), i.e. the percentage reduction of heat flow caused by the fabric under the specified test conditions. The thickness of each fabric under a definite load per square centimetre was measured by means of an instrument previously described$^{(3)}$. The air permeability and percentage hole-area (light transmission) were also determined. The thermal insulating values when plotted against thickness presented a series of points which were found to lie on a band on either side of a straight line which did not pass through the origin. This diagram was taken as a basis of discussion and it was suggested that the deviation of the points from the mean line is due to the differences in air permeability and light-transmission, which allow different amounts of air and of radiant heat to pass through the fabrics. In the previous paper on thermal transmission of fabrics this suggestion was not applied to the results obtained except in a general way. The object of the present paper is to test the validity of this suggestion in the light of the results obtained and to discuss the theories which may be involved.

---

* This paper forms part of a thesis approved for the degree of Doctor of Philosophy in the University of London.

It should be noted that, throughout, hygroscopic equilibrium is assumed, and thus no heat is transferred by evaporation at the warmer, and condensation at the cooler, places.

§ 2. EXPERIMENTAL RESULTS

The results recorded for various fabrics in the previous papers have been examined to find the effects of air permeability and percentage hole-area (as measured by light-transmission) on the total heat-flow. As the fabrics were different in structure, material, emissivity and surface roughness (which is thought to cause increased convection from the surface), it is not to be expected that the thickness, hole-area and air permeability cited above will explain the whole of the phenomena of heat-transmission. This conclusion was confirmed for single results or groups of results, and no definite conclusions could be reached in this way.

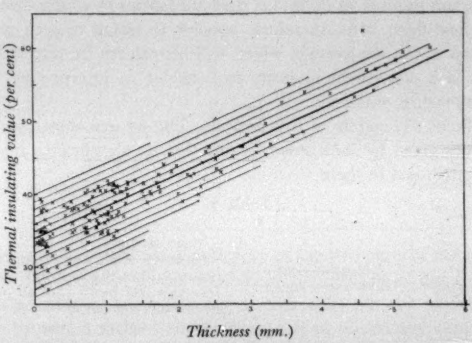


Figure 1.

As a fairly large number of results were available (about 130) it was decided to use a statistical method for their treatment. It was very necessary, however, to exercise caution in avoiding the employment of groups containing very small numbers of results. The thermal insulating values were plotted against the thickness, and this diagram, figure 1, formed the basis of the analysis. The best straight line was drawn through the points by the simple method due to Awbery(4). This method consists essentially in finding the "centre of mass" of all the points and then determining what might be called the "mean gradient"* of the line joining each point to the centre of mass. The "best" line has a gradient equal to the value so obtained, and passes through the centre of mass.

---

* For the actual process used in finding the mean gradient, reference should be made to Awbery's paper.

Such a line was drawn on the diagram and a series of other lines parallel to it were added at regular intervals, dividing the points up into groups according to their distance from the best line. If the theory suggested above for heat flow and its dependence on air permeability and hole-area is correct, the fabrics corresponding to the points lying in the lowest groups should have the highest permeability and percentage hole-area, and *vice versa.* Each point was therefore identified to its corresponding fabric and recorded in its appropriate group together with the full particulars of the fabric represented by it.

On taking the mean permeability and light-transmission for each group, the general trend of the results could be seen. It was found that intervals of 1 per cent in thermal insulating value gave erratic means and were therefore too small, but intervals of 2 per cent were satisfactory. Larger intervals would have given too few groups.

The best line may be considered as the relation between thermal insulating value and thickness for average fabrics. The other lines parallel to it relate to fabrics which, for a given thickness, differ in thermal insulating value from an average fabric by a certain number of units; i.e. they are fabrics in which there is a certain difference in heat-flow. It is, therefore, possible to assign to each group a mean excess heat-flow above the average which will henceforth be referred to as *excess heat flow.* It is a convenient quantity to consider in interpreting the physical meaning of the results obtained.

Table 1 shows the results of this analysis. The figures shown in brackets are the mean values given by such small groups that no significance beyond general trend can be attributed to them.

Table 1

Interval (in thermal-insulating-value units)	Excess of heat-flow above mean (W.)	Mean air permeability of all points within the interval (cm.^{3} per cm.^{2} per sec. per cm. head of water)	Mean percentage light-transmission of all points within the interval
− 8 to − 6	·538	(915)	(36·2)
− 6 to − 4	·385	680	17·9
− 4 to − 2	·231	230	8·4
− 2 to 0	·077	104	4·2
0 to 2	− ·077	99	4·2
2 to 4	− ·231	79	4·2
4 to 6	− ·385	(28)	(4·6)

The full-line curves in figures 2 and 3 show the relation between excess heat-flow and air permeability and percentage hole-area respectively. They show that there is a definite increase in heat-flow with increase in these quantities. Thus the early suggestions as to the curves of the variations of the points from the mean line on the (thickness, thermal insulating value) curve were feasible.

An attempt to analyse the result in the reverse way, i.e. by taking groups of values of the air permeability and percentage hole-area and finding the mean error from the best line for each group, was not so useful as it gave one or two very large groups and several very small ones. This method therefore is not considered here.

The most distinctive feature of the curves is that each is made up of two parts of very different gradients. This is especially marked in figure 3, which shows that for several groups the average percentage hole-area is practically constant. The increase in heat-flow in this part must therefore be due wholly to the air currents through the fabrics. It will be seen from figure 2 that in this region there is approximately a linear relation between the excess heat-flow and air permeability.

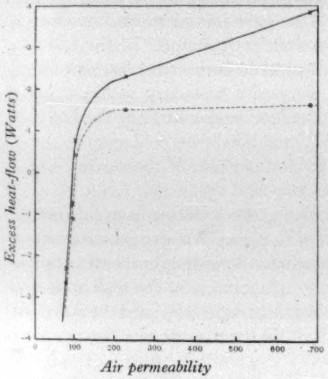


Figure 2.

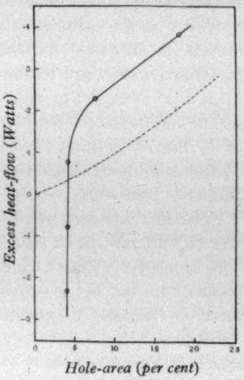


Figure 3.

It is necessary to explain the significance of the two parts of the curves and the very pronounced change in gradient, which is too great to be due to experimental errors. It is possible to suggest many mechanisms, but the one given below is the only one by which the author has been able to obtain any explanation of the bends in the curve.

§ 3. DISCUSSION OF RESULTS

In the curves for excess heat-flow against air permeability and hole-area respectively, shown in figures 2 and 3, the effects of air-flow and radiation are combined. It is necessary to separate these two effects. The radiation effect will be treated first, as its effects are more simply calculated and hence the air permeability effect may be deduced.

Suppose a hot body is giving off R units of heat per second towards a cold boundary in front of which is a screen pierced with holes amounting to n per cent of its area, and which has a temperature intermediate between the two. It is then obvious that $nR/100$ units of heat per second are transmitted directly through the

R
n

holes in the screen to the cold outer boundary. Gregory$^{(5)}$ has shown that as regards radiation a fabric behaves very nearly like a black body, so that for insulators such as these the small amount of radiant heat which may pass through the fabric, suffering one or two reflections in the process, is not significant. Attention may therefore be confined to direct transmission through the holes. The heat transmitted is proportional to the percentage hole area n, and R will subsequently be shown to be also a function of n. As far as could be ascertained the literature contains no records of work, either theoretical or practical, on radiation from a body through a perforated screen to a cold boundary. The following method of consideration has therefore been adopted. If a hot body is radiating heat in an enclosed space, the distance of the colder boundary walls of such enclosure from the radiating body has no effect on the quantity of heat radiated. The outer boundary can therefore be moved for purposes of calculation to any convenient position. In the case of a perforated screen and the outer boundary considered here, it is possible to bring them into coincidence and so produce a composite boundary with patches at screen and boundary temperatures. If the absolute temperature of the hot body be T_0, that of the inner surface of the screen T_1, and that of the cold outer boundary T_2, the conditions obtaining will be that ($100 - n$) per cent of the surface is at T_1 and n per cent at T_2.

T_0, T_1
T_2

Two methods may be considered for calculating the radiation from this surface. The radiation might be calculated from the fourth power of the mean temperature. This is incorrect since each element of area radiates according to its own absolute temperature and not in proportion to the mean temperature of the total area. It is therefore necessary to consider each infinitesimal area separately, and the individual radiations should then be summed and meaned. In the present case this process is simple and gives

$$R = SE\sigma\left\{T_0^4 - \left(\frac{100-n}{100}\right)T_1^4 - \left(\frac{n}{100}\right)T_2^4\right\} \qquad \ldots\ldots(1)$$

E, σ, S

where E is the emissivity, σ the Stefan-Boltzmann constant and S the area of the radiating surface. This expression (1) assumes that the insulator and the outer boundary are both equivalent to black bodies, which assumption is true in this case. Thus the heat transmitted directly by radiation through the holes is

$$\frac{nR}{100},\ \text{which} = \frac{nSE}{100}\sigma\left\{T_0^4 - \left(\frac{100-n}{100}\right)T_1^4 - \left(\frac{n}{100}\right)T_2^4\right\}.$$

The two unknowns in this equation are E and T_1. It is possible to obtain approximate values of the emissivity by a consideration of the heat-loss by radiation from the bare cylinder, which can be calculated from Stefan's law. Taking σ as $1{\cdot}36 \times 10^{-12}$ cal./cm.^{2}-sec. and the cold boundary at 12° C., i.e. according to the conditions of experiment, table 2 has been calculated for a black inner cylinder.

Table 2

Temperature-difference (° C.)	0°	5°	10°	15°	20°	25°	30°
Temperature of inner cylinder (° C.)	12°	17°	22°	27°	32°	37°	42°
Heat-loss, calculated (W.)	0	1·17	2·39	3·68	5·05	6·48	7·96

Thus for a temperature-difference of 25° C., the heat lost by radiation if the cylinder was black was 6·48 W. Curves were given in the author's previous papers for total heat-loss from the cylinder when the cold receiving surface was bright, and alternatively when it was black. At 25° C. the curve shows that the difference between the total heat-flows in the two cases amounts to about 2·7 W., and this must all be due to radiation; and since only radiation is affected by surface conditions this factor accounts for at least 2·7 W. It is not likely to account for much more, so that the emissivity may be taken as $2{\cdot}7/6{\cdot}5 = 0{\cdot}42$. This is of the same order as that obtained for paints with metallic bases$^{(6)}$.

The only unknown quantity left from the equation above is T_1, and since it is unlikely to be below 25° C. or above 35° C., a mean value of 30° C. or 303° K. has been taken for purposes of calculation. The difference from such a value is relatively small. The calculated values are shown by the dotted curve in figure 3, which indicates nothing which would account for the bend in the excess-heat-flow curves.

Attention must therefore be directed to the (excess heat flow, air permeability) curve in figure 2. Since the relationship between the radiation effect and percentage hole-area is known, the radiation through the holes for each group can be calculated from the mean percentage hole-area. By subtraction of this value from the excess heat-flow, the effect due to the air permeability can be found. The result is shown on the dotted curve in figure 2. The distinct bend of the curve still remains, and it is therefore in this part of the excess heat-flow that the explanation of this bend is to be sought.

In considering the flow of heat by convection through the fabric, it is first necessary to know the general form of the air current through the fabric. A model was therefore made consisting of two concentric tubes of the same diameter as the original apparatus, but only 8 cm. long. One end of the pair of tubes was closed by a metal plate and the other by a glass window, all joints being made airtight. The fabric was supported on a cylindrical metal framework which was mounted concentrically with the other cylinders and made air-tight contact at its ends with the metal plate and window respectively. Thus there was no passage for the air between the inner and outer annular spaces except through the fabric. After the inner cylinder had been heated from the inside for some time, puffs of smoke were admitted at various places near the inner cylinder, and the paths of the smoke were carefully watched. The general impression of the observations is shown diagrammatically in figure 4. The continuation of the smoke streams in the space between the inner cylinder and the fabric could not be very well observed, owing to the fact that there is another convection system of a similar nature in this space, and it is impossible to separate the two.

It has been suggested that a convection system of the type illustrated could not be obtained if the inner and outer cylinders had uniform temperatures throughout their circumferences. While this may be strictly true, the differences in temperature between the various parts of the cylinders must be very small owing to the thickness of the walls and the methods of heating and cooling.

As the air percolates through the fabric, there is a transfer of heat between the air-stream and the solid insulator, and it will now be shown that the bend in the curve is due to this interchange of heat. In the attempt to do this mathematically two difficulties are at once encountered. One is that the exact law of heat-transfer from the air to the solid is not known. The other is that, if a simple law be assumed, the number of variables depending on each other renders the integration difficult. The present discussion is therefore not quantitative. It has been shown that the convection results in an outward flow of air through the upper part of the fabric, which is in the form of a horizontal cylinder in the experiments, and an inward flow through the lower part. It may also be safely assumed that the temperature of the fabric is between that of the cool air coming to the hot cylinder from below and that of the heated air leaving the cylinder at the top. Considering first the upper half, we note that the effect of the heat-transfer here is to cool the air and thus to diminish the total heat flowing out from the hot cylinder. In the lower half, the effect of the heat-transfer is to heat the air stream. This means that there is an increase in heat flowing *towards* the hot cylinder, which again is equivalent to a diminution of heat flowing away from the cylinder. It is clear, therefore, that in both halves of the fabric, as the transfer of heat between the air stream and fabric becomes larger, the total heat-flow will become smaller.

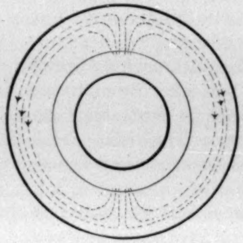


Figure 4.

The effect of the heat-transfer on the fabric must also be considered, since the total heat-flow depends to some extent on the temperature of the fabric. The consideration given above shows that the upper half of the fabric will be heated and the lower half cooled as a result of the heat-transfer. The two effects will thus neutralize each other to a large extent.

In the case of textile fabrics, those of open texture (i.e. having a large number of holes and therefore a high value for light transmission) possess high permeability for air. The stream of hot air can thus pass directly through such holes without impedance, and hence the transfer of heat from the hot air to the insulator will be small, since the facilities for heat-transfer will be small. As the degree of such perforation decreases, as indicated by decreasing values of percentage hole-area, there comes a critical point when direct transmission of air is no longer possible, so that in percolating through the material the air will follow a more or less devious path through the interstices. In this way the heat-transfer from moving air stream to fabric is greatly increased. If the texture is made still closer and therefore the hole-area still further decreased below this critical value, then obviously the heat-flow through the fabric should be less than that indicated by extrapolation from the part of the curve showing higher permeability values. It would therefore be expected that these two sets of conditions, more or less gradating into each other, which are obtained on either side of the critical value, will be indicated in the curve for air permeability and excess heat-flow by a distinct bend. In figure 2 such a bend actually does occur and is seen in the neighbourhood of 150 cm.^{3} per sec. per cm.^{2} per cm. head of water pressure.

Inspection of fabrics has shown that, in general, those whose permeabilities are higher than 150 units exhibit distinct holes in the texture, whilst those below this value rarely allow any direct transmission of light.

The change in the slope of the air permeability curve as indicated above is therefore attributed to the change in the mode of heat-transfer between the stream of air and the material, when the closer structure of the fabrics interferes with the free air-flow so that it changes its mode of percolation from direct to devious. Thus in consideration of heat-flow through air-permeable substances, the mutual influence of heat conditions and interchange of heat between the pervious fabric and the air stream is of importance.

Awbery(7), in a discussion of heat-conduction through a granular substance dispersed in a medium of different conductivity, refers to the effect of heat-interchange between the two components. He states that this interchange would cause deviation from certain relatively simple laws, but gives no mathematical analysis of the effect. This is a parallel case to that discussed in the present paper.

§ 4. HEAT-LOSS FROM THE BARE CYLINDER

In the discussion given in the previous section, it has been assumed that convection and radiation play a considerable part in the transfer of heat between the hot inner and the cooler outer cylinders. In order to check the validity of this assumption, the heat losses from the bare cylinder by conduction, convection, and radiation have been calculated. The results are shown in the curve, figure 5, from which it will be seen that the convection and radiation effects are both larger than the conduction effect. There can be no very great change in the relative magnitude of these effects when a fabric is introduced, and hence the assumptions used in this paper may be taken as justifiable. A few words are appended on the calculations.

The conduction was calculated from the concentric-cylinder formulae, with a value of the thermal conductivity at 25° C. interpolated from those given by Kaye and Laby at 0° C. and 100° C. As the conduction is proportional to the temperature-difference θ a straight line may be drawn through the origin and any calculated point. θ

The only available information(6, 8) relating to convection from horizontal cylinders assumes that they are in an infinite volume of the cooling medium. In the present case, however, the cylinder is enclosed concentrically in another nearly $2\frac{1}{2}$ times its diameter. With such an interspace there will be an approach to free-air conditions. The results of calculations made on that basis, however, will probably be too large, since the air approaching the cylinder will not have cooled down to the temperature of the outer tube. The heat-loss by convection from a horizontal cylinder has been found by many workers to be proportional to the $\frac{5}{4}$-power of the temperature-excess above the surrounding air, and also to the area of the cylinder. The factor in the equation connecting the heat-loss with these quantities depends on the diameter of the cylinder, and from a table given by Griffiths and Davis a curve has been plotted from which it was deduced that, for a cylinder-diameter of 5·50 cm., the above-mentioned factor has a value of $5{\cdot}3 \times 10^{-5}$. Table 3 shows values calculated thus for the heat loss by convection for various temperature differences.

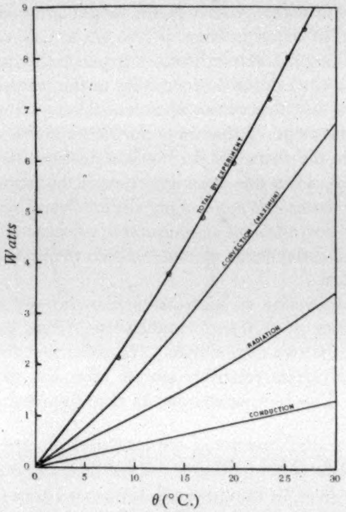


Figure 5.

Table 3

Temperature-difference θ (° C.)	1	5	10	15	20	25	30
Heat-loss by convection (W.)	0·096	0·72	1·70	2·91	4·04	5·35	6·72

A similar table has already been given for the heat-loss by radiation, and these figures, multiplied by the emissivity which was found to be about 0·42, are plotted in figure 5 along with the conduction and convection values. Figure 5 also shows the total heat-loss found by experiment as being rather less than the total of the three calculated components. This no doubt is largely due to the actual convection value being less than that calculated, owing to the assumptions regarding free-air conditions being hardly realized.

When the logarithm of the total heat-loss is plotted against temperature-difference it is found to give a straight line. The slope of this line would indicate that total heat-loss is proportional to $\theta^{1\cdot 20}$.

§ 5. ACKNOWLEDGMENT

The author wishes to thank the Research Control Committee of the Wool Industries Research Association for permission to publish this paper.

REFERENCES

1. Marsh, M. C. *Proc. Phys. Soc.* **42**, 570 (1930).
2. Marsh, M. C. *J. Text. Inst.* **22**, T 245 (1931).
3. Marsh, M. C. *J. Sci. Inst.* **6**, 382 (1929).
4. Awbery, J. H. *Proc. Phys. Soc.* **41**, 384 (1929).
5. Gregory, J. *J. Text. Inst.* **21**, T 57 (1930).
6. Griffiths, E. and Davis, A. H. "Transmission of Heat by Radiation and Convection." *D.S.I.R. Food Investigation Special Report*, No. 9. (Revised edition, 1931.)
7. Awbery, J. H. *Phil. Mag.* **12**, 1152 (1931).
8. *Dict. App. Phys.* **1**, "Heat, Convection of."

DISCUSSION

Mr J. H. Awbery. The paper gives a very interesting analysis, but I suggest that it may have read too much into the data. What is really known about the thermal insulating value as a function of permeability, after correction for radiation effects, is shown in the dotted curve of figure 2.

Consider now the apparatus set up without any fabric. There would be convection currents carrying heat from the inner to the outer cylinder. If a very open net of fabric is now inserted, it will make but little difference to the currents, and therefore to the heat-transfer. This is precisely what is found above permeabilities of about 170 units. Now reduce the permeability further, by using a finer mesh, and the currents are damped. They will carry less heat from one cylinder to the other, and this conclusion is quite independent of any knowledge of the detailed mechanism of heat-transfer at the fabric itself. The deduction is quite in accord with the curve, figure 2, and whilst it is independent of any considerations relative to heat-exchange at the fabric, it by no means proves that Mr Marsh's further conclusions are wrong. It only appears to render them superfluous.

Author's reply. Mr Awbery's explanation of the effect of air permeability on the thermal insulating value of a fabric is one that naturally occurs on the inspection of the dotted curve in figure 2. It assumes, however, that fabrics which have a permeability above 150–170 units are open nets which have little or no effect on convection currents, while those below have a much closer structure which causes the currents to be damped. This arbitrary division is certainly not supported in practice. Many quite "solid" fabrics have a higher permeability than this, and to be termed a net a fabric would have to have a permeability of at least 1000 units. I should like to quote two experimental results to show that high-permeability fabrics can affect the convection currents and hence the heat flow. In the course of the smoke experiments described in the paper, a fabric with a permeability of about 800 units was used and this was found to have an effect on the convection currents which could be very easily observed. Further, I have shown that when a very open wire gauze cylinder (91 per cent. hole area) was inserted, the total heat flow was reduced by 3 per cent. The permeability of the gauze would be practically infinite. I regret therefore that I cannot agree that the explanation of the bend on the dotted curve of figure 2 is as simple as Mr Awbery suggests.

621.318.35

A COMPACT ELECTROMAGNET FOR GENERAL PURPOSES

By L. F. BATES, Ph.D., F.Inst.P., Reader in Physics,
AND
B. J. LLOYD-EVANS, M.Sc. (Eng.), M.I.Mech.E.,
University College, London

Received December 22, 1932, *and in amended form January* 30, 1933.
Read February 17, 1933

ABSTRACT. An electromagnet suitable for many branches of research work is described. Special attention is paid to the construction of the coils, which are cooled by the circulation of oil. Some tests and experiments with a magnetic potentiometer are described.

---

§ 1. INTRODUCTION

An electromagnet was required for the investigation of the thermal and magnetic properties of ferromagnetic substances. Enquiry showed that few standardized magnets suitable for research purposes are made in England, whilst the present cost of many magnets of foreign manufacture is prohibitive. It was therefore decided to make the magnet here described, the construction being carried out in the Engineering Workshop at University College, London, by kind permission of Prof. E. G. Coker, F.R.S.

While it is not suggested that the design of the yoke and pole pieces of this magnet is particularly original, it is thought that some details of its manufacture will be of interest to other workers. At the same time it is felt that the effective arrangements made for the cooling of the magnetizing coils warrant some detailed description of them.

§ 2. DETAILS OF CONSTRUCTION

The constructional details of the magnet are given in figure 1. The yoke and pole-pieces, shown in figure 2, were of forged dead mild steel supplied by The English Steel Corporation, Sheffield. The steel was remarkably soft and easy to machine, having a Brinell hardness number of 110. The relevant magnetic data, obtained with a ring specimen of this steel, are given in table 1.

Table 1.

H (Gauss)	2·5	5·0	10·0	20·0	30·0	40·0	50·0
B	4900	9300	12300	13600	15500	16200	16600

The yoke was first planed all over and the holes for the pole pieces were bored. These two holes were finished at one setting with a broad tool acting practically as a scraper, the yoke being carried from the saddle of a lathe. The pole pieces, 4 in. in diameter, were then fitted to the bores by lapping.

The pole-tips are held to the pole pieces by central bolts which may be replaced by tubular bolts for certain experiments in magneto-optics. The use of separate pole-tips is not ideal from the point of view of prevention of magnetic leakage, but is necessary to allow of the provision of different shapes and special alloys for these tips.

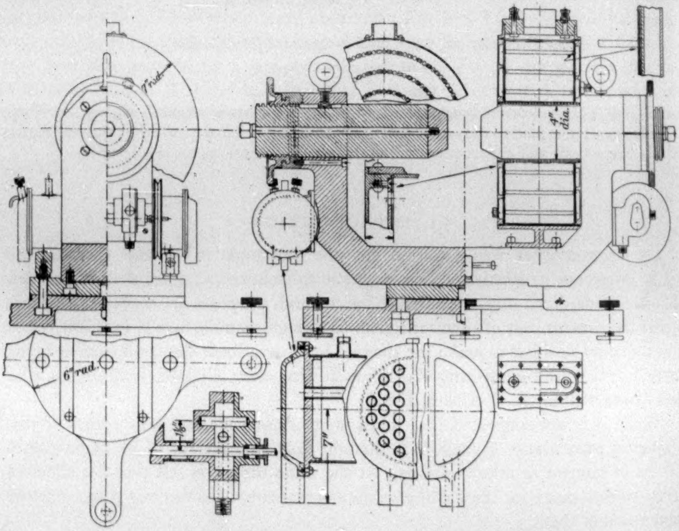


Figure 1. General arrangement and details of electromagnet.

The ideal shape for a fixed pole piece is, of course, a taper, but it was decided to make cylindrical pole pieces so that the width of the air gap might be more easily adjustable. A square thread, five to the inch, was cut on the outer end of each pole piece, engaging with a knurled brass handwheel held axially by a split cast-iron distance ring. The maximum axial adjustment on each pole piece is 2 in. A circular scale graduated in 200 parts on each handwheel allows the setting to be controlled to 0·001 in.

To prevent the pole pieces from turning, the lower ends of the eye-bolts, seen in figure 2, are machined to fit into holes in phosphor bronze keys engaging in suitable keyways in the pole pieces. These keys also limit the amount of the travel,

PROPERTY

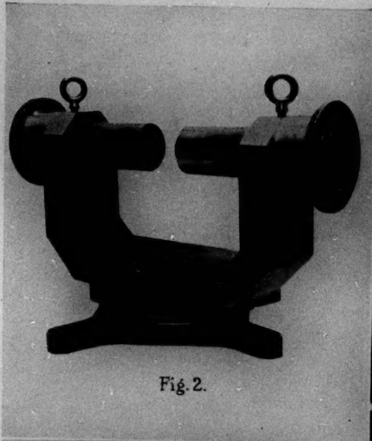
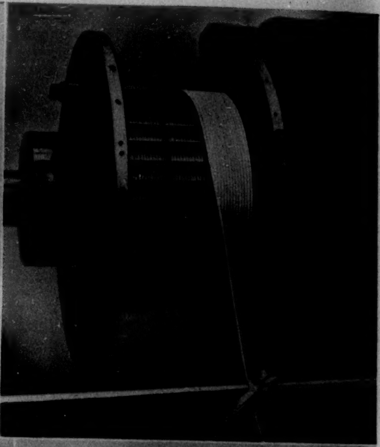


Fig. 2.



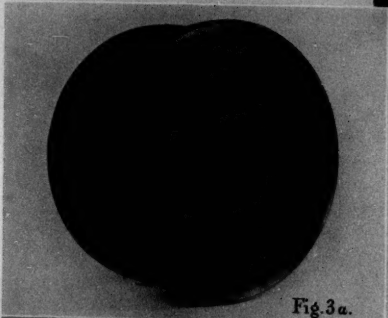


Fig. 3a.

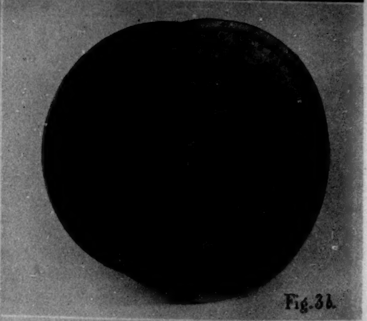


Fig. 3b.

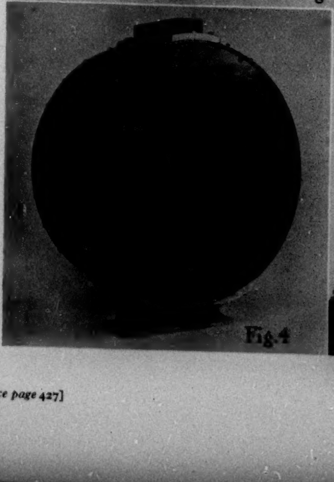


Fig. 4

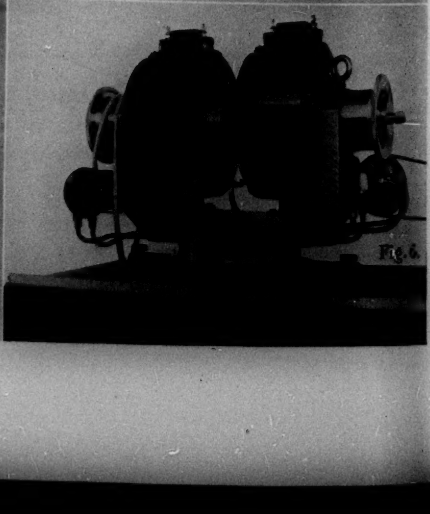


Fig. 6.

and the handwheels are kept comparatively small to prevent the keys or surfaces from being scored in case any foreign matter finds its way between the sliding surfaces. A half turn of an eye-bolt serves to lock the position of the corresponding pole piece. To preserve the micrometer adjustments of the handwheels from unnecessary wear, it is not intended that adjustment of the air gap should be made when the current is flowing.

Turntable. For certain experiments on crystals it is necessary to rotate the magnet through a measured angle about a vertical central axis. The yoke is therefore mounted on a cast-iron base-plate turning on a central pin in the manner of the slide-rest of a lathe. The amount of rotation is measured with a scale and vernier seen in figure 2 and made by Messrs Vinter, Dyer's Buildings, Holborn, W.C. 1.

The upper and lower plates of the turntable bed over the outermost $\frac{3}{8}$ in. only, in order to reduce friction to a minimum, with the result that the whole magnetic system can be rotated comfortably by hand.

Magnetizing-coils; formers. Each coil former consists essentially of a central brass tube carrying two annular side cheeks, or boxes of brass, and enclosed by a copper wrapper plate so as to form a drum. This is oil-tight except at the uppermost part, where a well is formed, and through which the two electrical leads are taken.

In the actual design, to save time in pattern-making, the cheeks of the formers were built up, but experience showed that the outer sections of the cheeks could be more easily constructed in the form of castings. This improved design is therefore incorporated in figure 1. The whole of the coil former was built up and fitted, and the appropriate portions were tinned before any wire was wound on. Thus the only joints to be made after the wire was in place were the circumferential joints between the wrapper plate and the outer rings of the side cheeks.

On reference to figures 3*a* and 3*b* which, of course, are pictures of the built-up former, it is seen that in the inner plate of each cheek there are three concentric rings of holes and a spacing ring. The latter prevents the radial flow of oil as described below, and as seen in figure 3*a*, to which reference is now made.

The oil is led in by a duct, seen in figure 4, to the innermost set of holes from which it flows axially, i.e. parallel to the lines of magnetic induction, to the opposite cheek through passages seen in figure 5 and described below. It now flows radially to the middle set of holes seen in figure 3*b*, and, further radial flow being prevented by the spacing ring, the oil now passes through these holes, axially crossing the windings to the middle set of holes in the first cheek, shown in figure 3*a*. It now flows radially to the outermost set of holes, and thence again axially across the windings to reach the outer annulus of figure 3*b*. From here it flows through a duct, not visible in figure 4, to the cooling system.

The insulation of the former consists on one side of a single disc of Paxolin $\frac{1}{16}$ in. thick, while on the opposite side three discs are used. The outer pair here are each $\frac{1}{16}$ in. thick, while the central disc is only $\frac{1}{64}$ in. thick, being cut away radially for a width of $1\frac{1}{4}$ in., to admit the passage of a strip of copper, $\frac{1}{64}$ in. thick, which acts as the electrical connexion or ingoing lead to the innermost layer of the coil. The insulation over the central brass tube consists of a cylinder of Paxolin $\frac{3}{32}$ in. thick, split axially as it had to be put in position in halves.

In the course of the manufacture, the inner brass plate of one of the side cheeks was marked off and the sets of holes, each $\frac{1}{4}$ in. in diameter, were drilled at one setting in all four brass plates and the eight Paxolin discs. As may be seen from figures 3*a* or 3*b*, no holes are drilled opposite the ingoing lead. The holes in the side cheeks and the corresponding insulation are kept in line by a tubular bushing in one of the holes.

The formers have an internal axial length of $5\frac{3}{8}$ in. and a radial dimension of $4\frac{1}{2}$ in.

Winding of the coils. It was decided to use double-cotton-covered copper wire of no. 12 s.w.g., so that with a current of 20 A. a total of about 61,000 ampère-turns is available. The winding was put on in uniform layers until it lay flush with the inner edges of any one of the three sets of holes. Axial bars of red fibre, $\frac{3}{8}$ in. × $\frac{3}{16}$ in. in section, were then placed between corresponding pairs of holes in the two cheeks of the former in order to leave an axial set of passages for the oil. The bars were held temporarily in position by thread as shown in figure 5, and more turns were wound on.

When the final layer was in place a turn of red fibre sheet $\frac{1}{16}$ in. thick and $5\frac{3}{8}$ in. wide was wrapped around the completed coil in order to protect the winding from heat during the soldering of the wrapper plate. The final layer of wire failed to extend right across the former, so as to ensure that the last turn was almost vertically below the outgoing terminal to the coil. Both terminals were mounted in a hollow block of teak fitted in the brass well, which served to accommodate to some extent the expansion of the oil when the latter became heated.

Each coil has its own gear wheel, pump and section of the cooler, as shown in figure 1, the pumps being driven by an external motor. The relief taps shown at the top of the cooler allow for the release of any air collected in the cooling system, and for the release of oil, in case the level rises too high in the well at the top of the coil.

Transformer oil, B30, supplied by the Vacuum Oil Co., was used, but before each former was filled, dry air was drawn through the path normally taken by the oil, a heating current of some 5 A. being maintained through the coils to remove as far as possible any moisture from the cotton insulation; this precaution is most essential. Each former contained approximately one gallon of oil, and this was forced through the cooling system about once per minute.

Each coil contains approximately 125 lb. of wire, and the total weight of the magnet and its attachments is about 600 lb. The complete magnet is shown in figure 6.

§ 3. PERFORMANCE

The magnet can be operated at 20 A. for considerable periods. Some idea of its performance may be gained from the following details. In table 2 are given the values of the axial field mid-way between two flat pole-tips, tapered from 9·7 to

8·4 cm. in diameter, with a gap of 1·5 cm. between them and the stated currents supplied to the coils.

Table 2

Current (A.)	1·0	3·5	5·0	8·0	15·0	23·0
Field (G.)	2776	9030	11100	13200	15250	16710

With the same pole-tips and a constant current of 20 A., the field mid-way between them varied with the width of the gap as set forth in table 3.

Table 3

Gap (cm.)	1·035	1·81	4·005	7·015	10·30
Field (G.)	19110	15060	9750	6620	4836

With the same pole-tips and a constant current of 20 A. the variation of the axial field with position in the gap was investigated. Some results for stated gaps are given in table 4.

Table 4

Gap (cm.)	Axial field at pole surface	Axial field mid-way between poles
4	9835	9780
6	7890	7500
8	6890	5990
10	6400	4925

With conical pole-tips, having an included angle of 120° and base 4 in. in diameter, whose ends were flat over an area 1 cm. in diameter, a mean field of 32,500 G. was obtained over an area of 12·6 mm.^{2} when the gap was 0·5 cm. and a current of 20 A. was employed.

Flux-losses. To obtain a measure of the flux-losses, a single loop of insulated wire was wound tightly on the yoke, or on the pole piece, and was connected to a flux-meter. The reading of the latter was recorded when the magnet current was reduced from 20 A. to zero, allowance being made for residual magnetism. With flat, non-tapered, pole-tips 0·85 cm. apart the data of table 5 were obtained when the loop was placed along the pole piece at the stated distances from the gap, i.e. from the pole-face.

Table 5

Position of loop (cm.)	0·05	1·0	2·0	3·0	4·0	5·05
Total flux through loop (Maxwells × 10^6)	1·406	1·525	1·604	1·653	1·693	1·757

When the loop was in position at 5·05 cm. it was as close as possible to the coil-face. Consequently, in these tests, the ratio of the flux crossing the gap to the flux crossing the iron just at the exit from the coils was 0·80. The total flux over each portion of the yoke inclined at 45° to the horizontal was 2·18 × 10^6 Maxwells. When the data of table 5 are plotted the graph obtained shows a point of inflexion for the loop in the position 2·5 cm. from the pole-face. This distance is practically equal to the distance at which the minimum value of H_x, shown in figures 7 and 8, occurs.

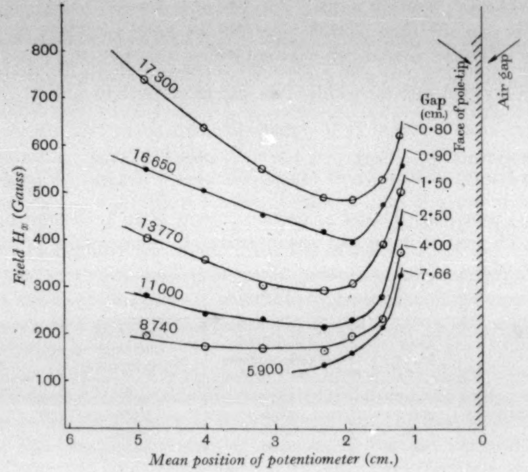


Figure 7. Variation of H_x with position on the pole piece. Plane pole-tips. Gap adjusted.

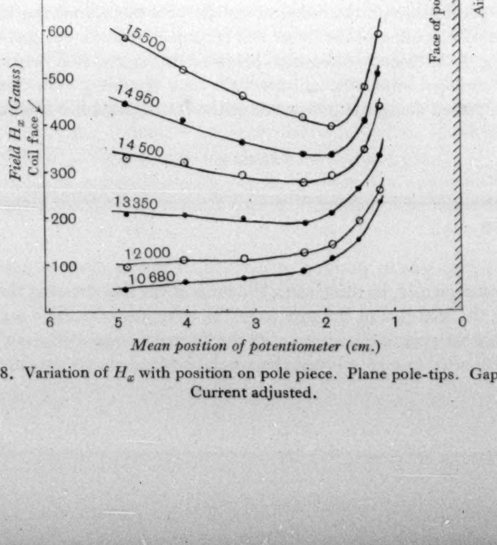


Figure 8. Variation of H_x with position on pole piece. Plane pole-tips. Gap 1·18 cm. Current adjusted.

Tests with a magnetic potentiometer. Some further interesting information was obtained by the use of a simple form of magnetic potentiometer*. This was made by taking an ebonite rod 5 mm. in diameter, with a small hole running axially through it, and winding upon it a solenoid of fine enamelled wire for a length of about 5 cm. To protect the wire a layer of cotton thread was wound upon the solenoid, and the ends of the solenoid and the cotton were secured with touches of hard wax. The ebonite rod was now placed in hot water and the portion on which the solenoid was wound was bent into a semicircular arch around a reel. On removal from the water, the ends of the ebonite rod were pushed through two holes in a small ebonite plate, so that the ends of the semicircle were flush with the lower surface of the plate. The semicircular piece, or half-ring, of ebonite was then cemented in position.

The wire of those portions of the solenoid which projected beyond the lower surface of the plate was unwound until the lowest turn on each side was flush with this surface. Any surplus ebonite rod was carefully filed away. The wire from one end of the solenoid was then threaded through the axial hole in the ebonite, so that the ends of the solenoid were now close together. These ends were cemented into a groove cut in the side of the plate, and stouter wires, to serve as leads, were soldered to them.

It was found advisable to remove as much as possible of the portions of the plate outside the semicircle, so that one could clearly gauge the outer limits of the solenoid. Thus, finally, a magnetic potentiometer consisting of a uniformly wound coil of semicircular shape, with about 450 turns each about 20 mm.^2 in area, was obtained, the external diameter of the ring being 2·4 cm.

The ends of the coil were connected to a sensitive moving-coil ballistic galvanometer of long period, and the potentiometer was used to measure the field actually acting upon various portions of the yoke and pole pieces. The potentiometer was placed on a part of the magnet where the field was to be measured, with the lower surface of the ebonite plate immediately in contact with the iron, and with the axis of the solenoid in the same plane as the direction of the field on the iron. On sudden removal of the potentiometer to a field-free region a deflection of the galvanometer resulted. This deflection was a measure of the difference in magnetic potential between the two points in the iron immediately below the centres of the lowest turns on the solenoid, and, therefore, of the mean field in the region between these points; in what follows this field is denoted by H_x. The potentiometer was H_x
calibrated by removing it from a uniform magnetic field, such as existed between flat pole-tips when a small current flowed through the magnet coils, the field being measured by a flux-meter.

With the pole-tips 8·4 cm. in diameter, a gap of 1·043 cm. and a current of 20 A. through the magnet coils, giving a field of 18,800 G. in the gap, the value of H_x over the horizontal portions of the pole pieces at a mean distance of 4·5 cm. from the edge of the gap was 356 G. On the middle of the sloping portion of this pole-tip, the value of H_x parallel to the sloping metal face was 750 G., while on the middle of the vertical portion of the yoke it was 130, on the inclined portion of the yoke 69, and on the middle of the base about 5 G.

---

* Cf. W. Wolman, *Arch. Elektrot.* **19**, 385 (1928). W. Rogowski and W. Steinhaus, *Ibid.* **1**, 141 (1912). A. P. Chattock, *Phil. Mag.* **24**, 94 (1887).

With flat pole-tips 10 cm. in diameter, a gap of 0·93 cm. and a current of 20 A. giving a field of 15,000 G. in the gap, the base value of H_x was about 3 G. With these tips we also obtained the sets of curves shown in figures 7 and 8. In figure 7 are plotted the values of H_x for various mean positions of the magnetic potentiometer along the horizontal portions of one of the pole pieces, the current being usually maintained at 20 A. and measurements made with a series of gaps. The vertical line on the right of the figure represents the edge of the pole-tip, and the line on the left represents the face of the coil. The field in the gap is recorded for each curve.

It was impossible, without using a much smaller potentiometer, to obtain values of H_x for regions nearer the gap. Indeed, in using the instrument close to a gap some skill in effecting the sudden removal was necessary, or the potentiometer would have been plunged into the huge field around the gap and false readings would have been obtained. Again, in fields which were very non-uniform the inevitable slight lack of uniformity in the winding of the potentiometer produced marked effects; the deflections on opposite sides of zero showed considerable differences in some cases. Mean values were always taken. Therefore it is not suggested that these curves are highly accurate. It is considered, however, that they give an interesting picture of the way in which the field actually acting upon the pole pieces varies, and that the results should be of assistance in choosing alloys for special pole-tips.

Figure 8 shows how the field on the pole piece varied with position when the gap was kept fixed and the current in the magnet coils adjusted to give different values of the field in the gap. In both figures 7 and 8 the curves for high fields in the gap show very pronounced minima. The minima disappear completely when the fields in the gap are small. The curves suggest that with a magnet such as is described here, pole-tips of alloys of high permeability should be at least 3 cm. thick for the production of most intense fields.

These measurements were checked with another potentiometer of slightly larger span, wound with two layers of wire, in all about 900 turns. The differences between readings on opposite sides of zero were much more pronounced than for the first potentiometer, but, on plotting the mean values as before, we obtained identical curves.

§ 4. ACKNOWLEDGMENTS

The authors have already recorded their indebtedness to Prof. Coker; it remains for them to thank Mr T. Gurman of the Engineering Workshop Staff for his excellent workmanship in the construction of this magnet, and also Mr L. Walden of the Physics Departmental Staff who furnished the photographs reproduced above.

One of the authors (L. F. B.), also desires to record his deep appreciation of a grant from the Government Grants Committee of the Royal Society, which covered the entire cost of the magnet, and of the facilities in the Physics Department afforded him by Prof. E. N. da C. Andrade.

DISCUSSION

Mr R. S. WHIPPLE said that the method of cooling seemed to be efficient and might serve for other instruments also. He asked what magnetic flux was attainable?

Mr J. GUILD enquired how the magnetic flux compared with that of an electromagnet of the du Bois type for the same size of gap?

Prof. A. O. RANKINE asked what was the saving in cost of production effected by the authors?

Dr L. F. BATES. The maximum flux so far obtained is 32,500 Gauss with a gap of 0·5 cm. between conical pole-tips having an included angle of 120° and base 4 in. in diameter, the ends being flat over an area 1 cm. in diameter; obviously, this flux could have been greatly increased by reducing the width of the air gap. The values of the magnetic flux compare very favourably with those recorded for a large magnet of the du Bois type. An interesting table of the comparative performances of several different types of electromagnet will be found in the latest edition of Müller-Pouillet's *Lehrbuch der Physik*, **4**, 418. We have not attempted to establish records, but have made a magnet which we consider particularly suitable for use in certain researches that one of us has in hand, and very suitable for general purposes. The approximate cost of the magnet was £100, of which £50 was expended on labour; the saving was therefore estimated to be about £150, overhead charges being, of course, very small.

535·371·07:535·312

THE SPURIOUS RING EXHIBITED BY FLUORESCENT SCREENS

By J. V. HUGHES, A.R.C.S., B.Sc.

Received December 21, 1932. *Read, with demonstration, February* 17, 1933.

ABSTRACT. The spurious ring exhibited by fluorescent screens used for the observation of electrons is explained as being due to total internal reflection of the light at the upper surface of the glass block of the screen. The theoretical intensity-distribution is deduced and is compared with experiment by the use of a specially designed photometer. The experimental results agree well with the theory.

Fluorescent screens used for the observation of electrons always show a ring round the bombarded spot, known as "the spurious ring." In general this ring has a very sharp inner edge, and gradually fades away on the outer side. It is usually explained as being due to light from the central spot which has suffered internal reflection in the glass and has returned to the material of the screen, whence it is scattered by the particles in all directions.

According to this theory, the inner edge of the spurious ring corresponds to the ray which is just totally internally reflected at the upper surface of the glass.

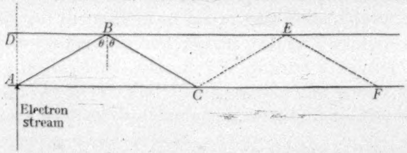


Figure 1.

According to this theory, light from the point of bombardment *A*, figure 1, is totally internally reflected at *B*, and strikes the material of the screen again at *C*, whence it is scattered in all directions. Thus, no matter in what direction the screen be viewed, the point *C* is observed bright. Rotation of the diagram about *AD* produces the spurious ring of radius *AC*.

Some of the light scattered from *C* is again internally reflected, as at either *B* or *E* in the diagram: in fact every point (such as *C*) on the first spurious ring gives rise to another complete ring round that point. The envelope of these secondary rings is a circle round *AD*, of radius *AF*. This is a possible explanation of the second spurious ring which is sometimes seen, but the sharpness of the second ring, when it is observed, would lead one to think that some of the light is not scattered at *C* but regularly reflected up to *E*, whence it is reflected again to *F*, where it is scattered by the particles of the screen. This explanation of the second spurious ring leads one to expect a sharper second ring than one would expect from the first explanation, and makes it easier to account for the third spurious ring which is sometimes observed.

If θ be the angle of reflection, D the diameter of the spurious ring, and t the θ, D, t
thickness of the glass, then $AC = \frac{1}{2}D$ and clearly $\tan\theta = D/4t$.

But for the critical angle of total internal reflection $\sin\theta = 1/\mu$ where μ is the μ
refractive index of the glass.

Thus
$$\mu = \operatorname{cosec}\tan^{-1}\frac{D}{4t} = \frac{4t}{D}\sqrt{\left(1 + \frac{D^2}{16t^2}\right)}.$$

Thus a measurement of D and t gives us a value of μ. These measurements were carried out for four screens, the thicknesses being measured with a micrometer screw gauge and the diameters of the rings by means of a pair of dividers.

To check the theory, the refractive indices of the glass blocks used for the screens were obtained in the usual way, by focusing a microscope first on the material of the screen, seen through the glass, and then on the upper surface of the glass, and thus getting the apparent thickness T of each of the screens in turn. The true T
thickness t being already known, the refractive index was obtained from the relation

$$\mu = \frac{t}{T}.$$

In all cases the refractive indices of any one screen, as obtained by these two separate methods, agreed to within the limits of experimental error.

The results are given in the table. Screen A was willemite floated on in waterglass solution. Screens B, C, D, were zinc blendes spread on with a solution of Canada balsam in xylol.

	Screen A	Screen B	Screen C	Screen D
Thickness t (cm.)	0·84	0·78	0·765	0·77
Ring-diameter D (cm.)	3·1	2·7	2·6	2·6
μ from these	1·47	1·53	1·54	1·55
μ from optical method	1·50	1·51	1·52	1·51

Two points of interest remain. One is that the light, after its one internal reflection, is able to reach the material of the screens (which is of course outside the glass block) and be scattered by it. The scattering material must therefore be in good optical contact with this second (lower) surface. The explanation of this lies in the fact that the material of the screen is held in position by an adhesive, either waterglass or Canada balsam, in which the particles of the screen are embedded. For the purposes of the light, these adhesives constitute practically an extension of the glass (as both materials have refractive indices of about the same value as that of glass) so that the particles of the material of the screen are optically in the glass, and hence can be acted on by the light.

The second point is to see whether theory can predict the approximate intensity-distribution, and particularly the sharp inner edge of the ring. In carrying out this investigation three assumptions are made: (*a*) The particles are sufficiently separated from one another as not to interfere with each other. Thus a cosine law of distribution of energy with angle is not involved. (*b*) The particles emit light in all directions. This is rather doubtful, but allowance for the deviation would be rather difficult, and the error introduced by making this assumption will probably have little effect on the shape of the intensity curve. (*c*) The light re-radiated from the ring of course contributes light to other parts of the screen. This secondary effect is taken to be negligible.

ϕ n We apply Fresnel's formulae, which for reflection at an angle ϕ in a material of refractive index n can be written:

$$A_3 = A_1 \frac{n^2 \cos\phi - \sqrt{(n^2 - \sin^2\phi)}}{n^2 \cos\phi + \sqrt{(n^2 - \sin^2\phi)}}$$

$$B_3 = B_1 \frac{\cos\phi - \sqrt{(n^2 - \sin^2\phi)}}{\cos\phi + \sqrt{(n^2 - \sin^2\phi)}}$$

$, B_3, A_1, B_1$ I where A_3, B_3, are reflected amplitudes due to amplitudes A_1, B_1, plane polarized perpendicular to and in the plane of incidence respectively. If I be the reflected intensity for unpolarized light

$$I = A_1^2 \left\{ \left(\frac{n^2 \cos\phi - \sqrt{(n^2 - \sin^2\phi)}}{n^2 \cos\phi + \sqrt{(n^2 - \sin^2\phi)}} \right)^2 + \left(\frac{\cos\phi - \sqrt{(n^2 - \sin^2\phi)}}{\cos\phi + \sqrt{(n^2 - \sin^2\phi)}} \right)^2 \right\}.$$

θ Here n is the refractive index of the glass in the direction of travel of the light, so that if θ be the critical angle of total internal reflection, $\sin\theta = n$, and for values of ϕ greater than θ we merely neglect the factors under the root signs and put,

$$I = 2A_1^2.$$

From figure 2, $\tan\phi = r/2t$,

$$\text{whence } I = A_1^2 \left\{ \left(\frac{2n^2 t - \sqrt{\{n^2 (r^2 + 4t^2) - r^2\}}}{2n^2 t + \sqrt{\{n^2 (r^2 + 4t^2) - r^2\}}} \right)^2 + \left(\frac{2t - \sqrt{\{n^2 (r^2 + 4t^2) - r^2\}}}{2t + \sqrt{\{n^2 (r^2 + 4t^2) - r^2\}}} \right)^2 \right\}$$

$$= A_1^2 f(r) \text{ say.}$$

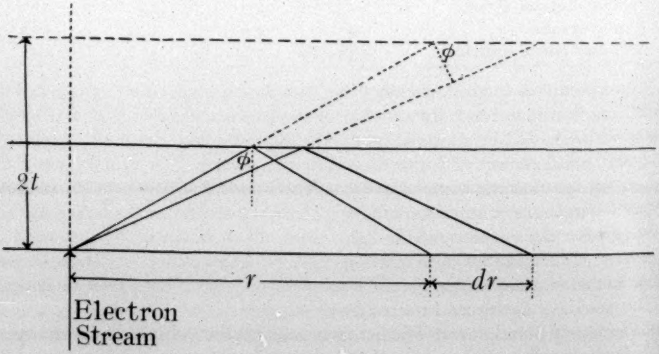


Figure 2.

The solid angle subtended by annulus of width dr at radius r is r

$$\frac{2\pi r\,.\,dr\,.\cos\phi}{AB^2},\text{ which }=\frac{\pi 2r\,.\,dr\,.\cos\phi}{t^2\sec^2\phi}$$
$$=\frac{2\pi r\,.\,dr\,.\cos^3\phi}{t^2}.$$

The area of the annulus is $2\pi r\,.\,dr$.

Thus if X per unit solid angle be emitted equally in all directions from A per second, the amount reaching this area per second, is X

$$X\,.\,2\pi r\,.\,dr\,.\cos^3\phi\,.\,f(r)/t^2,$$

where $f(r)$ is the function defined above to allow for the reflection. Thus energy per unit area per second, falling at radius r, is f (r)

$$X\,.\cos^3\phi\,.\,f(r)/t^2\text{ which }=\frac{X}{t^2}\left(\frac{4t^2}{r^2+4t^2}\right)^{\frac{3}{2}}f(r).$$

Substituting for $f(r)$ we get as a final expression that the intensity at radius r is proportional to

$$\left(\frac{1}{r^2+4t^2}\right)^{\frac{3}{2}}\times\left\{\left(\frac{2n^2t-\sqrt{\{n^2(r^2+4t^2)-r^2\}}}{2n^2t+\sqrt{\{n^2(r^2+4t^2)-r^2\}}}\right)^2+\left(\frac{2t-\sqrt{\{n^2(r^2+4t^2)-r^2\}}}{2t+\sqrt{\{n^2(r^2+4t^2)-r^2\}}}\right)^2\right\}.$$

Putting $n=1/1\cdot5=0\cdot667$ and $t=0\cdot77$ cm., we get the theoretical curve shown in figure 3. The maximum, where $r^2=n^2(r^2+4t^2)$, occurs at $r=1\cdot378$ cm., or a spurious-ring diameter of 2·76 cm. When r exceeds this value, i.e. when $r^2>n^2(r^2+4t^2)$, we take the intensity as being proportional to $2/(r^2+4t^2)^{\frac{3}{2}}$.

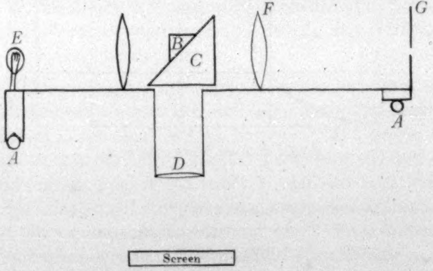


Figure 3. The photometer.

The inner edge of the curve rises extraordinarily steeply, and the fall away on the other side is gradual, in qualitative agreement with the observed effect. To test the agreement quantitatively, a photometer was constructed so that it could slide on rails A, figure 4, parallel to the edge of the screen when the latter was in position on the apparatus. I am indebted to Mr Warburton for the design of this photometer and for the interpretation of the results obtained by its use.

A photometer cube was used and is shown in figure 3. Light from the fluorescent screen, rendered parallel by D, was totally internally reflected in C. Light from a small bulb E, after traversing a suitable colour-filter, was collimated and passed directly through C and B. The field was observed with a telescope FG. By suitable placing of the pinhole eyepiece G a bipartite field could be obtained. The intensity of illumination from the bulb E could be reduced by means of an absorption wedge whose position could be read on a scale.

The readings of the wedge for equal illumination of the two halves of the field were obtained for various settings of the photometer on its rails (read on another scale), i.e. for various distances from the centre spot. The law of the absorption wedge being known, these readings could be converted into intensities.

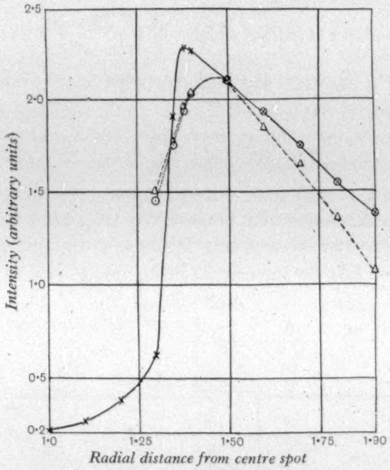


Figure 4.

×——× Theoretical curve
⊙······⊙ Curve corrected for finite scanning area
△-----△ Experimental curve

One correction has to be made. To obtain sufficient intensity, a large eyepiece-aperture was needed. Thus the intensity observed was not the intensity at a point but the mean over an area. The correction on this account is most readily effected by modifying the theoretical curve to allow for a finite scanning area, taken as circular. This correction also was carried out by Mr Warburton, and the theoretical curve, the modified curve, and the observed curve are all plotted on one sheet of graph paper in figure 4.

The experimental values, which are only relative, are adjusted to make the maxima coincide. The inner edge agrees well but the outer edge falls away more rapidly than the simple theory would indicate. Evidently, one of the assumptions made in the theory does not hold quite accurately.

Summing up, one can say that the theory of the rings here advanced—that they are due to reflection of the light emitted from the centre spot by the upper surface of the glass—seems adequate to account both for the size of and the intensity-distribution in the rings.

DISCUSSION

Mr T. B. Vinycomb. At the Physical Society's Exhibition a year ago one of the firms of apparatus-makers exhibited an arrangement for measuring the index of refraction of a slab of glass by means of this phenomenon.

Prof. G. P. Thomson. I think the author has done a neat piece of work. This effect is very striking and it is curious that it has not been more noticed in the literature. It might easily lead an experimenter who was unaware of it to false conclusions, but the method of photographic recording by the actual impact of the rays obviates the danger.

Dr W. D. Wright. Surely any doubt as to the cause of the spurious ring could have been removed by wetting the outer surface of the cathode tube. This would have increased the critical angle and hence the diameter of the ring.

Mr E. F. Fincham. The phenomenon described in this paper appears to be the same as the "halation ring" which is well known in photography. If a small source of light is photographed upon an unbacked plate and sufficient exposure is given, the image of the source is found to be surrounded by a flare and around this is seen a dark zone surrounded again by a bright ring produced in the same way as the effect described in this paper.

Mr J. Guild. The author has effectively traced to its source a phenomenon which appears to have been a mystery as well as an annoyance to workers in some branches of physics. I cannot help feeling, however, that a special *ad hoc* investigation of the cause of this halo ought to have been quite uncalled for. It is one of these simple and familiar phenomena, many of which are seen "by the wayside" in every laboratory, of which the explanations are so immediately obvious as to elicit no comment. The halo is not, as one might gather from this paper, specially associated with fluorescent screens. It is observed in every case in which there is a local concentration of light on a transparent plate with one matt and one smooth surface, as, for example, when a small image is focused on a sheet of ground glass or of flashed opal. The phenomenon is described, and its contribution to the behaviour of pot opal glasses investigated, in a paper by J. S. Preston*.

In so far as the halo is a nuisance to those experimenting in electron-diffraction it should be possible to work with an opaque screen and arrange the optical system so that the screen is viewed or photographed from the front.

---

* *Proc. International Illumination Congress*, **1**, 373 (1931).

Mr T. Smith suggested that the spurious ring could be easily distinguished if a non-parallel plate were used, non-concentric rings being then rejected.

Prof. A. F. Pollard. If these spurious rings are troublesome, may I suggest a construction of the fluorescent screen which would eliminate them. Make a collodion, or better a cellulose acetate, emulsion of the fluorescent crystals and cast a film on plate glass. Strip the film in the usual way by lowering the plate into water and pick up the film on the shellaced edge of a brass frame. As the film loses moisture it will contract and become taut. Paste a paper mask on the glass plate of the screen so as to leave a clear space of clean glass in the centre, and lower the film upon the paper edging which has been previously painted with shellac varnish. When the shellac is dry cut the brass frame free. The screen now consists of a thin collodion fluorescent film separated a few hundredths of an inch from the supporting glass plate, and internal reflections will not affect it. Diagonal airways must of course be cut in the paper edging to allow the escape of the air between film and plate during evacuation.

Author's reply. In reply to Mr Vinycomb: As far as I am aware, the theoretical intensity-distribution in the ring had not previously been deduced or compared with experiment. In reply to Prof. Thomson: It would be convenient if we could photograph the images on the screen from the outside of the apparatus, as then the vacuum need not be disturbed in plate-changing. The spurious ring renders this method of recording undesirable. In reply to Dr Wright: Unless a layer of water of thickness comparable with that of the block of glass were used, the increase in the diameter of the spurious ring would not be within the limits of experimental observation. In reply to Mr Fincham: The "halation ring" in photography appears to be due to the same cause as the ring here described. In reply to Mr Guild: The explanation of the phenomenon has usually been taken for granted, but it was considered desirable to verify our suspicions on the subject and demonstrate conclusively that our assumed explanation was correct. Using an opaque screen and viewing from the front involves viewing from that side of the screen which is in the vacuum. This involves viewing through an observation window, and at an angle with the normal to the screen, so as not to interfere with the beam. Whilst this suffices for settings preliminary to photographing, it is sometimes desirable to take measurements on the screen, which would be difficult with a screen viewed in this way. Mr Smith's suggested arrangement can be shown also to distort diffracted rings seen on the screen, and hence to render measurements on the screen unreliable. In reply to Prof. Pollard: The screen suggested suffers from the drawback that despite the airways through the paper edging, the collodion film would probably be sucked off the glass if the vacuum were turned on suddenly. As a matter of fact, in practice the spurious ring is not as troublesome as one would expect it to be from its intensity. This is probably due to the greater sharpness of the true diffracted rings and to the fact that the eye is more sensitive to sudden changes of intensity than to the actual magnitude of the intensity.

771.534.531.51

THE DIRECT RECORDING OF RELATIVE INTENSITIES BY MEANS OF A MICROPHOTOMETER

By N. THOMPSON, B.Sc., Physics Department, The University, Sheffield

Communicated by Prof. S. R. Milner, F.R.S., December 3, 1932, *and in revised form*
January 25, 1933. *Read February* 17, 1933

ABSTRACT. A description is given of an addition to the usual form of recording microphotometer, which gives a record on which ordinates are linearly proportional to light-intensities. Results are quoted to show that the performance of the instrument compares favourably with that of the unmodified form.

It is well known that with a recording microphotometer of the usual type a curve is obtained whose ordinates are not linearly proportional to the intensities of the light which caused the blackening of the photographic plate. By measuring the record a series of photographic densities are found, and a calibration curve, obtained by photometering a set of density marks, must be used to convert these into relative intensities. For the most accurate work, where areal rather than peak intensities are required, this involves measuring a number of ordinates for each line in the spectrum, converting to relative intensities, re-drawing the curve, and then obtaining its area with a planimeter. This is seen to entail an immense amount of work, which in the past has usually been prohibitive. As a result, peak intensities have been used even for comparing lines whose (unresolved) fine structure is different, and erroneous results have ensued. As a further result, practically no reliable information has been obtained on the relative intensities of bands in a band spectrum, where the peak intensity is of very doubtful significance. The apparatus to be described, when used in conjunction with such a microphotometer, gives a record which shows the relative intensities directly, and thus enables determinations of areal intensities to be made merely by using a planimeter. In addition, if a large number of lines are to be compared for which the same (intensity, density) calibration curve is applicable, the apparatus will greatly expedite the process, even when the peak intensities are used.

As a preliminary, we will define a quantity which is a measure of the amount of blackening of the photographic plate, and one which, for our purposes, is more convenient than the density d which is usually used. This density is defined as $\log (a_0/a)$, where a is the deflection of the recording galvanometer and a_0 is the maximum value of a, obtained when the light is traversing an unexposed part of the photographic plate. The quantity we will use is defined as $(a_0 - a)/a_0$, the symbols having the same meaning as before, and this we will refer to as the *blackening* b. The (intensity, blackening) calibration curve is very similar in shape

d

a, a_0

b

to the (intensity, density) curve, with the important difference that it is asymptotic to the line $b = 1$, instead of going off to infinity; see the plate, (*c*).

Suppose now we have an opaque screen, in which is cut a fine slit in the shape of an (intensity, blackening) calibration curve, and suppose the spot of light, after reflection from the mirror of the recording galvanometer, falls on this in the form of a fine line parallel to the axis of intensity (I). This spot is made to lie along the line $b = 1$ when undeflected, and along the line $b = 0$ when in the position of maximum deflection. Then at any instant its intercept on the axis of b will give the blackening of that part of the negative which is at that moment being photometered. Moreover, that portion of the light which emerges through the screen in the form of a small spot will have suffered a displacement, the component of which parallel to the axis of I will be proportional to the corresponding intensity. We therefore only require an optical system which will reproduce this deflection parallel to I on the revolving drum, while at the same time taking no account of the motion parallel to b, in order to produce a record on which the ordinates are proportional to intensities.

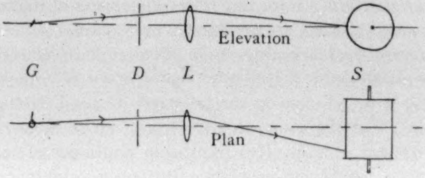


Figure 1. The optical system of the instrument.

Such a system is shown diagrammatically in figure 1. G is the galvanometer mirror, S the recording drum of the microphotometer, and D the pierced template described above. L is a special lens which is equivalent in its optical properties to two cylindrical lenses of different focal lengths, cemented together with the axes of the cylinders at right angles. As the axis of the recording drum which was to be used was horizontal, there was inserted between G and D an arrangement of two right-angled prisms cemented together (R, figure 2) which had the effect of making the galvanometer appear to deflect in a vertical plane. If the drum be made to rotate about a vertical axis, this arrangement can, of course, be dispensed with: it is shown in figure 2, but not figure 1. The template is placed with the axis of b vertical. In the vertical plane, L forms an image of G on S, so that however much the galvanometer deflects, the spot of light is always on the same horizontal line on S. In the horizontal plane, L has a shorter focal length, and D and S are conjugate foci, so that the movement of the spot on S is proportional to the horizontal component of its motion on D, as required.

In order to obtain an image of a slit on D, formed by a beam of light which has been reflected from the galvanometer mirror, the following arrangement is used, figure 2. A lens B forms an image of a small source of light P on the galvanometer mirror G. The light passes through a slit A, so placed that it and the template D

are also at conjugate foci of the lens B. Figure 2 shows the general layout of the whole apparatus. Calculations of the optical system, and repeated trials, showed that the following dimensions gave the best performance: $AB = 27$ cm., $BD = 138$ cm., $GD = 66{\cdot}6$ cm., $DL = 33{\cdot}3$ cm., $LS = 100$ cm.; the lens L has an aperture 4·5 cm. square, and its two focal lengths are 50 and 100 cm. A further item in the optical system, not previously mentioned, is a strip of cylindrical lens C, which is mounted in the box that houses S, and serves to concentrate the light into a finer spot on the drum. To enable the instrument to be used in its unmodified form if required, the lens L and the template D are mounted together on a geometrical stand, which enables them to be rapidly removed and replaced. The same applies to the double-prism system R, but the items P, A, and B remain permanently in position. When the unmodified form is required, a second source of light, placed near P, is used, and R is replaced by a single totally reflecting prism.

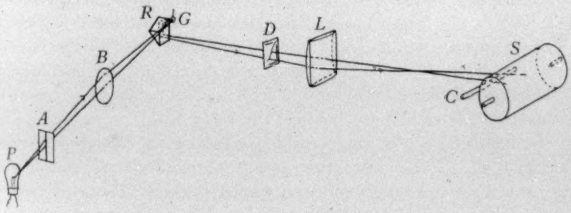


Figure 2. General lay-out of the whole apparatus.

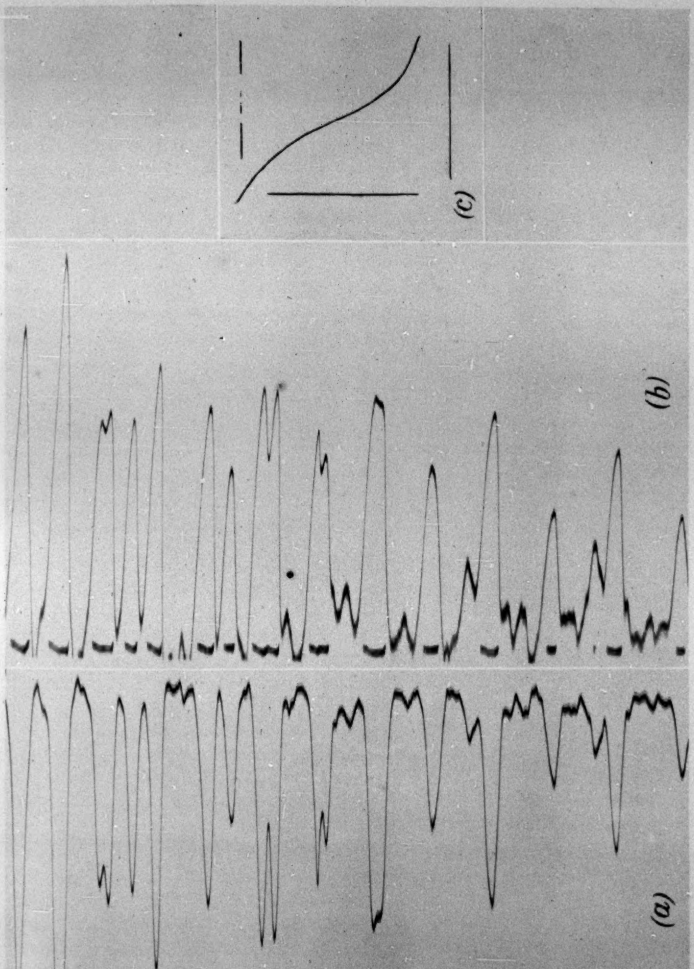
The method of manufacturing the template in the shape of the (intensity, blackening) curve is as follows. A set of density marks is obtained on the plate in the usual way and photometered with the normal form of the instrument, and the (intensity, blackening) curve is drawn on a suitable scale. A piece of aluminium foil is obtained, smoothed out by rubbing on a sheet of glass until the surface has a high polish, and thinly coated with paraffin wax. By means of a pantagraph giving a reduction of 1 : 5 this wax is then scratched off in the shape of the curve, and the foil is immersed in a bath of caustic soda. In about fifteen minutes the foil is etched completely through, leaving an edge which can be surprisingly sharp and smooth. To adjust the instrument for recording intensities, the template is clamped in a holder having screw-controlled traverse and tilting motions, and is moved until the undeflected line of light lies along the line $b = 1$. In order to make this adjustment the more accurately, a part of this line is etched through the foil, as are also parts of the lines $b = 0$ and $I = 0$. The appearance of the template is as shown in the plate at (*c*), which is a contact print of an actual template. The position of the template having been adjusted, maximum galvanometer deflection is obtained, and the magnitude of this is altered by means of a neutral-tinted wedge in the path of the microphotometer beam until the line of light lies along $b = 0$. The recording then proceeds in the usual way: the spot of light which passes through the slit in the template along $I = 0$ traces out on the record a straight line which gives the zero from which the intensities are to be measured. It occasionally happens that one template is found to be applicable to a number of photographs taken under similar conditions, but in general a separate template must be prepared for each plate photometered. If it is not desired to preserve the template, results almost as good can be obtained by using smoked glass instead of aluminium foil, with a consequent further saving in time.

The plate shows at (*a*) and (*b*) the results obtained by photometering the same negative, first with the normal instrument, and secondly by the above method. In order to test the accuracy of the method, a record of part of the iron-arc spectrum, obtained with the normal photometer, was measured up, and the relative intensities of some forty lines were obtained from a calibration curve. A template was prepared from the same curve and the relative intensities were also obtained directly. The values of the intensities of each line, as obtained by the two methods, were then plotted one against the other. The points should lie on a straight line through the origin, and by choosing suitable scales this line can be made to have a slope of 45°. The points were found to lie very close to the line, over a range of intensities from 1 to 14 in arbitrary units. As a measure of the errors, the root mean square value of the perpendicular distances of the experimental points from the (estimated) line of closest fit was calculated; this had the value 0·073, measured in the same units as the intensities. For purposes of comparison, a third record was taken which was an exact repetition of the first, and the correlation between the intensities as found from these two was found in a similar manner. The root-mean-square value of the deviations in this case, on the same scale as before, was 0·071. These figures, which do not represent unique results, serve to show that the addition of this device to a microphotometer does not in any way lessen the accuracy, which appears, in fact, to be limited mainly by the irregularities due to plate-grain. This same cause renders the adjustment of the maximum deflection a little uncertain, and an error in this direction shows up on the record as a non-coincidence of the two zeros (i) as given by the broken straight line caused by the light passing through the slit along $I = 0$, and (ii) as given by the level of the "troughs" in the record itself: see the plate. If the error is but small, it can be shown that the better approximation is given by using the broken straight line. Further, the accuracy is really greater than the above results would indicate; for it is no longer necessary to be content with peak intensities, and a glance at a record will show that the exact value of an ordinate is much more difficult to determine at a peak than elsewhere.

In conclusion, I would like to express my thanks to Messrs Priest and Ashmore, of Sheffield, who very kindly provided me with the double cylindrical lens used in this work.

DISCUSSION

Mr A. Harvey. Since the shape of the (intensity, blackening) curve is a function of the wave-length it would follow that the template can only be correct for one particular wave-length. It would be of interest to know the ranges over which the author has succeeded in working with the templates he has used.



Record of a photograph of the perturbations in the (1, 2) band of the negative nitrogen spectrum, obtained (*a*) with the normal instrument, and (*b*) with the modified form. The template was inserted in the holder in a reversed position, to make (*b*) the mirror image of (*a*). Also, the template (*c*) used to convert (*a*) into (*b*).

Di

de
tha
mo
ve
ca
sp
an
ap
th
a s
co
re
alt
ar
sc

a
th
m
th
si
bo

bo
sp
H
th
e

n
q
d
r
t
t
w
c
b
i
t

Mr J. Guild. There is no doubt that for many purposes this very ingenious device will prove both useful and efficient. It is desirable, however, to point out that if the spectrum under examination is produced with a prism spectrograph, areas measured on the author's records will not be proportional to energy except over a very short range of spectrum in which the variation of dispersion with wave-length can be neglected to within the order of accuracy aimed at in the work. If a greater spectral range is embraced the ordinates will require to be corrected for dispersion and the curves replotted before their areas are measured. Similar considerations apply to spectra produced with gratings of the echelette or echelon type in which the Fraunhöfer "spectra of the first class" (i.e. the diffraction bands produced by a single grating element) are relatively narrow. In fact, in the last-mentioned case, correction for the variation in intensity across the band is necessary however restricted the wave-length range under investigation. I am sure, however, that although it is necessary to bear these limitations in mind there are many cases arising in practice where the author's device will be of great assistance to spectroscopists.

Mr R. S. Whipple. I had the pleasure of seeing the author's device in Sheffield a few days ago, and was much impressed with the simplicity of his apparatus. As the instruments were arranged it was possible to change from one to the other method of recording in the course of a few minutes. I gathered that in practice the author generally uses a template made on smoked glass, and that this is a simple and satisfactory procedure. It greatly simplifies the technique, and may become the method that is generally employed.

Author's reply. In reply to Mr Harvey: The range over which a template can be used depends on the nature of the photographic plate and on the region of the spectrum being investigated. The author has made no tests himself, but Lochte-Holtgreven* obtained results which indicate that there would be little variation in the shape of the curve over a range of 60 Å. The range usually quoted in which errors due to this cause can be neglected is 20–30 Å.

While I do not claim, in the case of heterochromatic photometry, to have removed the necessity for correcting for dispersion, the procedure involved is not quite that indicated by Mr Guild. If it can be shown that the experimentally determined (intensity, blackening) curve has the same shape and size over a certain range of wave-lengths, no further correction for the variation of the dispersion in this range need be made. For suppose the dispersion at one end is twice that at the other. With a source of light in which the intensity I_λ is independent of the wave-length λ, the quantity of light per unit area of photographic plate at one end will be half that at the other, and thus the ordinates on the record will be halved. On the other hand, the abscissae will be doubled, on account of the increased dispersion, and thus the area will be unaffected. We might note in passing that in such a case peak intensities would lead to quite erroneous results.

---

* *Z. f. Phys.* **64**, 443 (1930 .

If the variation of the experimental (intensity, blackening) curve cannot be neglected, suppose we divide the range into a number of smaller regions in which this approximation can be made. We must now use a standard lamp for which the (I_λ, λ) relation is known. The spectrum of this lamp is photometered across at the mid-points of these sub-regions, and the peak intensities are noted. From the known (I_λ, λ) relation and the known dispersion the amounts of light falling on unit area of the photographic plate at the various points can be calculated. These will not agree with the peak intensities, owing to the varying plate sensitivity, and the ratios of the former to the latter will give a set of factors by which experimentally determined intensities in each sub-region must be multiplied in order to make them comparable with one another.

As was mentioned above, the size of these sub-regions is of the order of 20 Å, large enough to include the whole of a single band of most systems.

536.21:552.1

A METHOD FOR THE DETERMINATION OF THE THERMAL CONDUCTIVITIES OF ROCKS*

By H. A. NANCARROW, M.Sc., A.Inst.P., Research Student,
East London College

Communicated by Dr Allan Ferguson, November 28, 1932. *Read March* 17, 1933.

ABSTRACT. The rock specimens are turned as circular cylinders of diameter 5 cm. and height 2 cm., and are bisected by a cut made perpendicular to the base along one diameter. The top of the cylinder is heated and the temperature-gradient in the specimen is measured by means of thermocouples held in a mica holder inserted in the cut. The temperature-distribution and heat-flow in the specimen are each shown to be represented by a series containing Bessel and hyperbolic functions. Constants involved in the arguments of these functions are shown to be dependent upon the loss of heat from the hot surfaces exposed to the air in the apparatus. The determination of these surface heat-losses is described. Observations and results are given for four specimens.

§ 1. INTRODUCTION

The work described in this paper was undertaken at the suggestion of Prof. C. H. Lees with the object of developing a method for the determination of the thermal conductivities of rock specimens. It was intended that the apparatus should be of simple design and that the preparation of specimens should not involve drilling. The specimens were turned as circular cylinders about 5 cm. in diameter and 2 cm. in height; they were bisected by a cut along a diameter perpendicular to the plane surfaces.

The top of the specimen was heated, and the temperature-gradient in it in the steady state was measured with two thermocouples placed between the halves of the cylinder. From this gradient, the power input and the value of the total surface emissivity obtained in a separate experiment, the conductivity could be calculated.

§ 2. DESCRIPTION OF APPARATUS

The apparatus is shown in figure 1. It is made of copper, and stands in a wooden box which prevents draughts from affecting the readings. The thermocouples and power leads coming from the apparatus pass from the wooden box through small glass tubes. The base of the cylindrical copper chamber is about 9 cm. in diameter and 0·4 cm. thick. There is a circular, plane-topped, raised portion at the centre of the base upon which the specimen is fitted. The base carries three ebonite plugs *D*, *E*, *F*, each pierced by two small holes through which thermocouple wires are carried out, and the terminals connected to the heating-coil are mounted upon two further ebonite plugs *G*.

---

* Thesis approved for the Degree of Master of Science in the University of London.

Between the two semicylinders of rock, when they are upon the raised portion of the base, is a mica holder supporting two thermocouples, the wires of which are parallel to the base. A thin sheet of mica is cut to the same length as the perpendicular face of a semicylinder, but slightly higher, with one long edge straight. The best method was to use a safety-razor blade and a steel rule, the mica being laid upon a piece of plane glass. This piece of mica is then laid upon a short length of a metre scale, with the straight edge in contact with a straight glass edge fixed to the wood as shown in figure 2. The wires of the two thermocouples are then placed on the mica, parallel to the straight edge, with their junctions at the centre. The lines on the scale allow this to be done quite accurately by eye. The couples are held in position during the process of construction by small pieces of sealing-wax run on to the wooden holder. Parallelism of the straight edge and the thermocouples having been secured and then checked by means of a travelling microscope, a little seccotine is smeared carefully along each wire to fix it to the mica. This is allowed to harden, the rest of the slip is seccotined, and a second mica slip similar to the first is then laid upon the whole, with its straight edge in contact with the glass edge. A second piece of metre scale is placed upon the mica and a kilogram weight is then placed on the top of this, in order that the holder shall be flat and that excess seccotine shall be forced out. After a day or two such a couple-holder may be removed from the wooden former. The distances of the couples from the straight edge can be readily observed with a travelling microscope. The couple-holder is then gripped firmly in position between the halves of the specimen, with its lower edge in contact with a glass plate on which the halves rest, and its upper edge is trimmed to the height of the specimen by means of the razor blade. The holder is then ready for use.

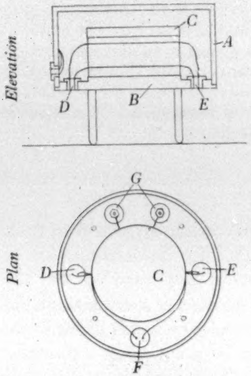


Figure 1.

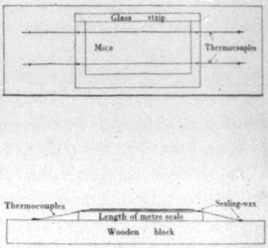


Figure 2.

It is fastened between the halves of the specimen by smearing glycerine upon its surface and the rectangular faces of the specimen. Glycerine is smeared upon the raised portion of the base and a very thin piece of mica is then placed upon this. The use of this piece of mica is explained below. The base of the specimen is also smeared with glycerine. It is then slid upon the mica. Thermal contact between the specimen and the heating-disc on it is secured in the same way.

The copper heating-disc is a cylindrical box 5 cm. in diameter and 0·5 cm. thick containing a heating coil of nichrome strip wound star-shaped on a mica ring and insulated from the disc with thin mica. The sides of the box are thick so that there is a wide surface of contact between the lid and the sides to ensure good transfer of heat. The lid is held down tightly by six countersunk screws. The ends of the nichrome strip are taken out radially through small glass tubes which just slip over the nichrome. The leads to the coil are of gauge-36 copper wire and are soldered to the nichrome at the points just before they enter the disc. The leads are taken to the two terminals mounted on the base.

The copper cap A, which is 0·25 cm. thick and 4 cm. high, fits tightly upon the base B. Thermal contact between the cap and the base is made by amalgamating the edges in contact. Thermocouples are soldered to the heating disc and the cap. That on the disc is formed by soldering a copper wire to one end of a diameter and a eureka wire to the other end. The couple fitted to the inside of the cap is placed halfway up and its leads are taken out through a small ebonite plug let into the side of the cap.

Thermocouples. The thermocouples are of gauge-36 copper and eureka wires. The junctions are formed by soldering the scarfed wires together, as fused junctions are very liable to fracture and are, in most cases, larger than scarfed joints. The cold junctions are made in glass tubes containing mercury, immersed in water in a large vacuum-walled 'food jar.' From the cold junctions copper leads run to a four-point mercury switch which enables the various couples to be connected to the potentiometer.

The couples were standardized with their cold junctions in a thermos flask containing ice. The hot junctions were enclosed in very thin glass tubes immersed in succession in the vapours of boiling carbon tetrachloride, water, and aniline and in water at air temperature contained in a thermos flask. The temperature of the water was read with a mercury-in-glass thermometer standardized at the National Physical Laboratory. The e.m.fs. obtained were read on a Cambridge Scientific Instrument Company thermocouple potentiometer and could be read to 1μV. The e.m.fs. obtained were used to construct curves of deviation from the standard e.m.f. tables given in the *International Critical Tables*. These deviation curves were then used with the standard e.m.f. table to find the temperatures. The couples in one mica slip were calibrated before being placed in the mica, and when in position were compared in an electric furnace with a calibrated thermocouple. At the temperatures used in experiments with the rock specimens the readings were found to be the same as when the couples were enclosed in thin glass tubes for calibration. The couples for the mica holders were therefore calibrated in thin glass tubes before being mounted, as this was more convenient.

Mention has been made of a thin sheet of mica placed between the base of the apparatus and the base of the specimen. Cross-coupling of the various thermocouples can be effected at the four-point switch, which is used to change from one couple to another and serves to check the insulation of the couple; the latter is generally good when the apparatus is first set up but a leak develops owing apparently to the glycerine hydrolysing on the mercury-copper surface at the base, where traces of a greenish solution appear. As a result, the glycerine on the mica holder served as a poor conductor between the lower couple leads and the base.

On insertion of the thin mica sheet the leak was no longer observed. Mention has been made of this as the author has not seen any previous reference to such an effect.

§ 3. THEORY

v We may consider the specimen to be a cylinder as in figure 4, where v represents z, r, θ the temperature-excess of the point z, r, θ over that of the enclosure. Considering a cylinder as above, we have the following boundary conditions.

When $z = 0$ $v = 0$,

" $z = b$ $v = V$,

" $r = a$ $-k . \partial v/\partial r = hv$,

h, k where h, k are respectively the emissivity and the conductivity of the material.

Laplace's equation in cylindrical co-ordinates

$$\frac{\partial^2 v}{\partial r^2} + \frac{1}{r}\frac{\partial v}{\partial r} + \frac{1}{r^2}\frac{\partial^2 v}{\partial \theta^2} + \frac{\partial^2 v}{\partial z^2} = 0.$$

Since the system is symmetrical about the z azis, the $\partial^2 v/\partial\theta^2$ term is zero.

It can be shown that the solution of this equation is

$$v = A' J_0(\alpha r) \cosh \alpha z + B' J_0(\alpha r) \sinh \alpha z,$$

A', B', α where A', B' and α are constants to be found from the boundary conditions and $J_0(\alpha r)$ is a Bessel function of zero order.

Since $v = 0$ for $z = 0$ the term involving the hyperbolic cosine disappears.

$$\therefore\ v = B' J_0(\alpha r) \sinh \alpha z.$$

At $r = a$,

$$-\frac{\partial v}{\partial r} = Kv,$$

where $K = h/k$, and, since

$$\frac{d}{dx}[J_0(\alpha x)] = -\alpha J_1(\alpha x),$$

we have

$$\alpha a . J_1(\alpha a)/J_0(\alpha a) = Ka,$$

$\alpha_1, \alpha_2, \alpha_3$ which has solutions α_1, α_2, α_3 etc. For the specimens used we can show that $\alpha_1 a = 0{\cdot}33$ approximately and $\alpha_2 a = 3{\cdot}85$, so that since $a = 2{\cdot}5$ cm.,

$$\alpha_1 = 0{\cdot}132, \qquad \alpha_2 = 1{\cdot}53.$$

v will be given by

$$v = \sum_{s=1}^{s=\infty} B_s' . J_0(\alpha_s r) \sinh \alpha_s z,$$

which we may write

$$v = \sum_{s=1}^{s=\infty} B_s . J_0(\alpha_s r) \frac{\sinh \alpha_s z}{\sinh \alpha_s b}.$$

We then have, since $v = V$ when $z = b$,

$$V = \Sigma\, B_s\, J_0(\alpha_s r).$$

It may be shown* that

$$B_s = \frac{2}{a^2} . \frac{1}{K^2 + \alpha_s{}^2} . \frac{VaK}{J_0(\alpha_s a)}.$$

Hence we have

$$v = \sum_{s=1}^{s=\infty} \frac{2}{a^2} . \frac{1}{K^2 + \alpha_s{}^2} . \frac{VaK}{J_0(\alpha_s a)} . \frac{J_0(\alpha_s r)}{1} . \frac{\sinh \alpha_s z}{\sinh \alpha_s b}.$$

Dropping suffixes and retaining B,

$$\frac{\partial v}{\partial z} = \Sigma\, \alpha B J_0(\alpha r) \frac{\cosh \alpha z}{\sinh \alpha b}.$$

The heat conducted over the entire cross section at a height z

$$= \int_0^a \Sigma \alpha B J_0(\alpha r) \frac{\cosh \alpha z}{\sinh \alpha b} . 2\pi r\, dr$$

$$= 2\pi k a\, \Sigma\, B \frac{\cosh \alpha z}{\sinh \alpha b} . J_1(\alpha a).$$

The heat flow across top surface $z = b$ is

$$2\pi k a\, \Sigma\, B \frac{\cosh \alpha b}{\sinh \alpha b} . J_1(\alpha a).$$

In an experiment we determine v_1 and v_2 at positions z_1 and z_2, r being zero in both cases, so that

$$v_1 = \Sigma\, B \frac{\sinh \alpha z_1}{\sinh \alpha b},$$

$$v_2 = \Sigma\, B \frac{\sinh \alpha z_2}{\sinh \alpha b}.$$

The heat flow across the top surface of the specimen is equal to the heat input to the heating-disc less the heat emitted from the top and sides of the disc. If we take V as the temperature-excess of the disc over the cap, S_0 as the area of the top and sides, and h_0 as the value of the total emissivity for the top and sides, the heat flow through the top surfaces is $(H - h_0 S_0 V)$ where H is the heat input to the coil.

V, S_0
h_0
H

Hence

$$H - h_0 S_0 V = 2\pi k a\, \Sigma\, B . \frac{\cosh \alpha b}{\sinh \alpha b} . J_1(\alpha a),$$

$$\frac{H - h_0 S_0 V}{v_1 - v_2} = 2\pi k a \frac{\Sigma\, B . \dfrac{\cosh \alpha b}{\sinh \alpha b} . J_1(\alpha a)}{\Sigma\, B . \dfrac{\sinh \alpha z_1 - \sinh \alpha z_2}{\sinh \alpha b}}.$$

---

* MacRobert, *Spherical Harmonics*, p. 283.

Taking, as a first approximation, the first term in each summation we have

$$\frac{H-h_0S_0V}{v_1-v_2}=\frac{2\pi ka\,.\,B_1\,.\,\dfrac{\cosh\alpha_1 b}{\sinh\alpha_1 b}\,.\,J_1(\alpha_1 a)}{B_1\,\dfrac{\sinh\alpha_1 z_1-\sinh\alpha_1 z_2}{\sinh\alpha_1 b}}$$

$$=\frac{2\pi ka\cosh\alpha_1 b\left(\dfrac{\alpha_1 a}{2}-\dfrac{\alpha_1{}^3a^3}{2\,.\,8}\right)}{2\sinh\tfrac{1}{2}\alpha_1(z_1-z_2)\cosh\tfrac{1}{2}\alpha_1(z_1+z_2)}$$

$$=\frac{\pi ka\cosh\alpha_1 b\,.\,\dfrac{\alpha_1 a}{2}\,.\left(1-\dfrac{\alpha_1{}^2a^2}{8}\right)}{\sinh\tfrac{1}{2}\alpha_1(z_1-z_2)\cosh\tfrac{1}{2}\alpha_1(z_1+z_2)}\qquad\ldots\ldots(1).$$

When α is small, this reduces to

$$\frac{H-h_0S_0V}{v_1-v_2}=\frac{\pi a^2k}{z_1-z_2},$$

giving k thus,

$$k=\frac{H-h_0S_0V}{\pi a^2}\,.\,\frac{z_1-z_2}{v_1-v_2}\qquad\ldots\ldots(2).$$

Having obtained this approximate value of k we can proceed to take into account two terms in each expansion.

$$H-h_0S_0V=2\pi ak\,\frac{B_1'\,.\cosh\alpha_1 b\,.\,J_1(\alpha_1 a)+B_2'\,.\cosh\alpha_2 b\,.\,J_1(\alpha_2 a)}{B_1'(\sinh\alpha_1 z_1-\sinh\alpha_1 z_2)+B_2'(\sinh\alpha_2 z_1-\sinh\alpha_2 z_2)},$$

B_s'

where

$$B_s'=\frac{2}{a^2}\,.\,\frac{1}{K^2+\alpha_s{}^2}\,.\,\frac{Vak}{J_0(\alpha_s a)}\,.\,\frac{1}{\sinh\alpha_s b}.$$

Cancelling out the common factor $\frac{2}{a^2}\,.\,\frac{VaK}{1}$ we have finally

$$\frac{H-h_0S_0V}{v_1-v_2}$$

$$=2\pi ak\,\frac{\dfrac{1}{K^2+\alpha_1{}^2}\,.\,\dfrac{J_1(\alpha_1 a)}{J_0(\alpha_1 a)}\,.\,\dfrac{\cosh\alpha_1 b}{\sinh\alpha_1 b}+\dfrac{1}{K^2+\alpha_2{}^2}\,.\,\dfrac{J_1(\alpha_2 a)}{J_0(\alpha_2 a)}\,.\,\dfrac{\cosh\alpha_2 b}{\sinh\alpha_2 b}}{\dfrac{1}{K^2+\alpha_1{}^2}\,.\,\dfrac{1}{J_0(\alpha_1 a)}\,.\,\dfrac{\sinh\alpha_1 z_1-\sinh\alpha_1 z_2}{\sinh\alpha_1 b}+\dfrac{1}{K^2+\alpha_2{}^2}\,.\,\dfrac{1}{J_0(\alpha_2 a)}\,\dfrac{\sinh\alpha_2 z_1-\sinh\alpha_2 z_2}{\sinh\alpha_2 b}}$$

$$\ldots\ldots(3).$$

From this equation k may be calculated to a second order of approximation.

Determination of the values of α_s. The quantities α_1, α_2, ... satisfy the equation

$$\frac{\alpha_s a\,.\,J_1(\alpha_s a)}{J_0(\alpha_s a)}=Ka.$$

Using tables of $J_0(x)$ and $J_1(x)$ we can plot values of $x\,.\,J_1(x)/J_0(x)$ against x, and then read off the values of x required to give α_1, α_2, etc. The values necessary for this are given in another paper by the author*. Further,

$$aK=ah/k,$$

---

* Page 462 of this volume.

and k is readily found from equation (2) while h is found by the method described later.

With the specimens used, the portions of the curve required for the determination of α_1 and α_2 are shown in figures 3*a* and 4*a* of the above-mentioned paper.

§4. DETERMINATION OF *h*

It will be seen that, in the theory given above, the heat-loss in cal./sec. at a surface S is taken as ShV where h is a constant and V is the temperature-excess over that of a surrounding enclosure. S, h, V

The method of finding h was to support the heating-disc in its usual position in the apparatus by means of a small glass tripod. Thermal contact between the legs of the tripod and the disc, and between the triangle of the tripod and the base of the apparatus, was maintained with glycerine films. Current was then passed through the heating coil and, after about an hour, the readings of the disc and cap thermocouples were taken at 10-minute intervals. When the difference of these readings was constant the final readings were used to find the value of h.

The heat lost from the disc was due partly to conduction down the glass tripod and partly to conduction down the thermocouple wires, in addition to that emitted from the surface by convection and radiation. The first two have, of course, to be allowed for.

In the case of the tripod we have to consider the conduction down three cylinders.

The dimensions of the tripod legs were:

length $d = 2{\cdot}2$ cm., d

cross-sectional area $q = 0{\cdot}04\pi$ cm.^{2}, q

perimeter $p = 0{\cdot}4\pi$ cm. p

Moreover $h = 0{\cdot}0003$, $k = 0{\cdot}004$, while

$$v = Ae^{\sqrt{(ph/qk)}.x} + Be^{-\sqrt{(ph/qk)}.x}.$$

At $x = 0$, $v = V$, so that

$$V = A + B \qquad \text{......(4).}$$

At $x = d$, $v = 0$, so that

$$0 = Ae^{\sqrt{(ph/qk)}.d} + Be^{-\sqrt{(ph/qk)}.d} \qquad \text{......(5).}$$

At $x = 0$,

$$\frac{dv}{dx} = \sqrt{\left(\frac{ph}{qk}\right)}(A - B) = 1{\cdot}23\,(A - B) \qquad \text{......(6).}$$

Hence from equations (4) and (5) we can find A and B, and using these values can find dv/dx and hence $-qk.dv/dx$ for each leg of the tripod.

To determine the correction for the heat flow along the thermo-wires we write $v = v_0 e^{-\sqrt{(ph/qk)}.x}$, where v is the temperature at a point on the wire distant x cm. from the disc. v_0, v, x

The heat conducted away from the disc by the wire per second

$$= -\,qk.dv/dx \quad \text{for} \quad x = 0$$
$$= \sqrt{(qk.ph)}.v_0.$$

For copper wire of gauge no. 36,

$$\sqrt{qk.ph} = 1\cdot1 \times 10^{-4}.$$

For eureka wire of gauge no. 36,

$$\sqrt{qk.ph} = 0\cdot3 \times 10^{-4}.$$

The total loss along the thermocouple leads is $1\cdot4 \times 10^{-4}.v_0$ cal./sec.

The heat input having been corrected by these means the value of h is given by

$$h = \frac{\text{Corrected heat input}}{(\text{Disc temperature} - \text{Cap temperature})} \cdot \frac{1}{\text{Total surface area of disc}}.$$

Readings were taken for various heat inputs. The results are shown graphically in figure 3. It will be seen that h is not constant but increases with increase of temperature-difference. Consequently in the calculation of k the value of h is read from the curve for a temperature-excess equal to the mean of the temperature-excesses indicated by the thermocouples in the mica slip. The error introduced by this procedure will be small, since equation (2) which gives k fairly accurately is independent of α.

§5. HEAT-LOSS FROM TOP AND SIDES OF HEATING-DISC

h_0

The value of h obtained by means of the above experiment is a mean of the values of the total emissivities of the top, bottom and sides of the disc. It probably corresponds very closely to the value for the sides, as it has been shown* that the ratios of the heat-losses by convection from the top, sides and bottom of a body in free air are roughly as $1 : \frac{3}{4} : \frac{1}{2}$. The value of h_0, i.e. the mean total emissivity of the top and sides, will of course be greater than the value of h which is found by the tripod method. Some idea of it may be obtained from the following considerations.

T_1, T_0

If we have a surface S with a temperature-excess V over that of an enclosure it will emit heat from the surface by radiation and convection. Then the heat emitted

$$= S\,[\sigma\,(T_1^4 - T_0^4) + hV],$$

T_1 and T_0 being the absolute temperatures of the surface and the enclosure, respectively; and

$$T_1 - T_0 = V.$$

Taking the figure for the emissivity of a dull copper surface, given by Griffiths and Davis*, we have

$$\sigma = 0\cdot15 \times 1\cdot36 \times 10^{-12}.$$

$\bar{h}$, S_1, S_2

In an experiment with the disc resting on a glass tripod we have heat being emitted from the top, sides and bottom, and, as has been said above, it has been shown that the values of the respective convection losses will be roughly as $1 : \frac{3}{4} : \frac{1}{2}$. Taking them as h, $\frac{3}{4}\bar{h}$, $\frac{1}{2}h$ we have, in a tripod experiment, if S_1 is the horizontal surface and S_2 is the vertical surface, that the heat emitted

$$= S_1\,[\sigma\,(T_1^4 - T_0^4) + \bar{h}V] + S_2\,[\sigma\,(T_1^4 - T_0^4) + \tfrac{3}{4}\bar{h}V] + S_1\,[\sigma\,(T_1^4 - T_0^4) + \tfrac{1}{2}\bar{h}V]$$

$$= \sigma\,(T_1^4 - T_0^4)\,(2S_1 + S_2) + \tfrac{3}{4}\bar{h}\,(2S_1 + S_2)\,V.$$

This in our calculations we put equal to $(2S_1 + S_2)\,h''V$, obtaining

$$h'' = [\sigma\,(T_1^4 - T_0^4) + \tfrac{3}{4}\bar{h}V]/V.$$

---

* *Food Investigation Board, Special Report*, no. 9.

From the top and sides of the disc would be emitted at the same time

$$S_1\,[\sigma\,(T_1^4 - T_0^4) + \bar{h}V] + S_2\,[\sigma\,(T_1^4 - T_0^4) + \tfrac{3}{4}\bar{h}V].$$

To find h_0, the mean value of the total emissivity for the top and sides, we put this equal to $(S_1 + S_2)\,h_0V$ so that

$$\begin{aligned} h_0 &= \{S_1\,[\sigma\,(T_1^4 - T_0^4) + \bar{h}V] + S_2\,[\sigma\,(T_1^4 - T_0^4) + \tfrac{3}{4}\bar{h}V]\}/(S_1 + S_2)\,V \\ &= [\sigma\,(T_1^4 - T_0^4)\,(S_1 + S_2) + \bar{h}V\,(S_1 + \tfrac{3}{4}S_2)]/(S_1 + S_2)\,V. \end{aligned}$$

$(T_1^4 - T_0^4)$ can be put equal to $4T_0^3\,(T_1 - T_0)$ if $(T_1 - T_0)$ is small compared with T_0.

In the experiments performed T_0 is approximately 290° K, so that

$$\sigma\,(T_1^4 - T_0^4) = 2 \times 10^{-5} \times V$$

approximately. Hence

$$\begin{aligned} h_0 &= 2 \times 10^{-5} + \bar{h}\,(S_1 + \tfrac{3}{4}S_2)/(S_1 + S_2), \\ h'' &= 2 \times 10^{-5} + 0{\cdot}75\bar{h}. \end{aligned}$$

Substituting in the expression for h_0 the values of S_1 and S_2 for the disc used we have

$$h_0 = 2 \times 10^{-5} + 0{\cdot}9\bar{h}.$$

Taking a value of h'' from the curve obtained from experiments with the disc upon the glass tripod we have at

$$\begin{aligned} V = 6^\circ\ \text{C.}, \qquad h'' &= 1{\cdot}3 \times 10^{-4}, \\ h'' = 2 \times 10^{-5} + 0{\cdot}75\bar{h} &= 1{\cdot}3 \times 10^{-4}, \\ \therefore \quad \bar{h} &= 1{\cdot}5 \times 10^{-4}, \\ \therefore \quad h_0 = 2 \times 10^{-5} + 0{\cdot}9\bar{h} &= 1{\cdot}6 \times 10^{-4}, \end{aligned}$$

i.e. h_0 is approximately 25 per cent larger than h''.

One might, therefore, obtain values of h_0 by adding 25 per cent to the values of h'' obtained from the tripod experiments. Any inaccuracies due to approximations in the above calculations would be of small importance, for with the specimens used the heat emitted from the heating-disc is only about 5 per cent of the heat input to the specimen. An error of 10 per cent in the value of h_0 would, therefore, result in an error of about ½ per cent in the value of k. It was thought that some experimental test of this view should be carried out. The method adopted was to coat the lower horizontal surface of the disc and the raised portion of the base of the apparatus with lampblack. This was done by holding them over the flame of turpentine burning on a piece of asbestos wool. A cylindrical paper tube was then constructed from drawing-paper. This tube was of the same height as the rock specimen and had a diameter slightly smaller than that of the disc. One edge of the tube was seccotined lightly and it was fixed to the base of the disc. The tube, with heating-disc fixed on the top of it, was then placed in position, as if it were a specimen, upon the raised portion of the base of the apparatus. The cap was, of course, fitted, current was passed through the heating-coil, and readings of the disc and cap couples were taken. It was found that readings could be taken fairly rapidly by raising the temperature quickly to a desired point and then reducing the current to the value calculated to give that temperature, readings then proceeding at 10-minute intervals for about 40 minutes.

The heat emitted from the top and sides was found by subtracting from the heat input to the coil, the heat conducted away by the cylinder of air, and that radiated from the base of the disc. The correction for the heat conducted down the cylinder of air was obtained by means of a calculation similar to those for the glass tripod, it being assumed that convection was absent when the heating-disc was uppermost. The heat radiated to the base was calculated from the formula

$$S\sigma\,(T_1^4 - T_0^4),$$

σ being taken for the lampblack surface as 0·9 of the value for a black body radiator.

The values of h_0 thus obtained are shown on the curve in figure 3. It will be seen that the values obtained lie on a curve which approximates to "a 25 per cent correction to h''" curve.

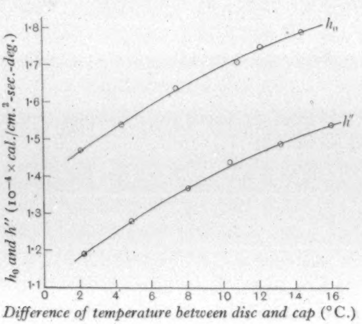


Figure 3. Values of h_0 and h''.

As the approximate calculations support the results obtained from the above experiments, the value of h_0 used in the calculation of the heat input to the specimen in the steady-state experiments was read off the h_0 curve obtained from those experiments.

§6. FULFILMENT OF THE CONDITIONS ASSUMED IN THE THEORY GIVING THE TEMPERATURE-DISTRIBUTION IN THE STEADY STATE

The theory given postulates a cylinder with an isothermal upper surface. The heating-disc, being of copper of fairly thick section and having quite a small diameter, complies with this condition. The other boundary condition, that the temperature of the base is equal to that of the enclosure, was tested by fitting another thermocouple to the base of the apparatus. As the apparatus was first constructed the contact between the cap and base was copper-to-copper; with this arrangement differences of temperature were observed. Upon amalgamating the surfaces of contact of cap and base these differences were greatly reduced and could be ignored at the temperatures used.

There is also the question of the effect of the couple-holder. The couple-holder, being surrounded by a much larger volume of rock, will tend to attain closely the temperature-distribution of the larger volume. Any slight differences would affect the reading of each couple in the holder by the same amount and the resultant temperature-gradient would remain unaltered. That the effect is extremely small was confirmed by the readings taken in some earlier experiments. In these the two semicylinders were cemented together with Keene's cement, thermocouples being embedded in the cement. These cement couple-holders were quite thick, up to 2 mm., and of course the thermal conductivity of the cement is different from that of mica. However, the temperature-gradients obtained with these cement holders were, to a close degree of accuracy, the same as those obtained with the mica couple-holders. Also, for a given specimen, the same values of k are obtained from observations taken with different mica couple-holders.

The influence of the mica couple-holder upon the quantity of heat flowing into the specimen, and the effect of the specimen not having a circular section, must also be considered. The heating disc is circular but the specimens are, of course, not truly cylindrical. They were originally turned as circular cylinders but when they were bisected the portion of the rock lost in the cutting rendered the specimen no longer cylindrical. Consequently the heating-disc has a small part of its lower surface which is not in contact with the specimen. Heat is emitted from this portion of the base of the disc to the enclosure.

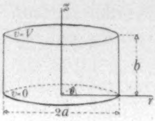


Figure 4.

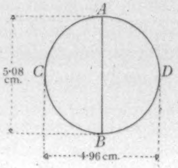


Figure 5.

In addition, there is the fact that the arrangement of specimen and slip constitutes two thermal resistances in parallel. In the case of specimen no. 3, figure 5, the heating-disc has a diameter of 5·08 cm., the couple-holder has a thickness of 0·04 cm., the area of the top of the slip is 0·20 cm², the area of the heating-disc is 20·27 cm², and the area of the specimen is 19·66 cm² The area of the lower surface of the heating-disc not in contact with the specimen is 0·41 cm² Taking a temperature-excess of 8° C. and $h = 0{\cdot}00013$ we have that heat is emitted from this area at the rate of 4×10^{-4} cal./sec. At this temperature-excess the heat input to the specimen is about 0·5 cal./sec. The correction which would have to be applied is small and is, therefore, neglected in practice. If it be assumed that $k = 5 \times 10^{-3}$ for the specimen and $k = 1 \times 10^{-3}$ for the couple-holder, the thermal resistance of 1 cm. of the specimen is 1/0·098 and of the couple-holder 1/0·0002.

The heat flow down the couple-holder would therefore be about $\frac{1}{5}$ per cent. In *a*

the calculations to find k it is neglected. In the finding of k from a set of steady-state observations the mean of the lengths AB and CD is taken as the value of a, the radius of the cylinder.

§7. EXPERIMENT AND CALCULATIONS TO FIND k

The apparatus is set up as described. The current is supplied by secondary cells. The current passing through the heating-coil is measured by finding the potential-drop across a resistance of 0·1 Ω in series with the heating-coil. This potential-drop is measured on the thermocouple potentiometer. The potential-difference at the terminals on the case is obtained by means of a potential-divider which reduces the p.d. to one thousandth of the value at the terminals. The resulting p.d. is then read on the thermocouple potentiometer. The power input at the coil terminals can thus be found accurately. The value of the heat input to the disc is obtained by correcting for the power lost in the copper leads and the heat flow along the leads of the disc thermocouple.

A high resistance, which can be smoothly changed by small amounts, is connected in parallel with the resistance regulating the current. This high resistance acts as a convenient vernier control for keeping a constant current. Small current-variations can be easily observed on the potentiometer and corrected with this device.

When the current has passed for about 2 hours, readings of the four thermocouples are commenced at 10-minute intervals. These are continued until the steady state is reached; this takes from about 1 to 3 hours, depending upon the power input. When the steady state has been reached the final readings then taken are used to calculate k. One such set of calculations is given for one specimen.

Specimen no. 3. Gabbro.

Current	e.m.f.	Thermocouple readings (mV.)				Cold-junction temperature
(A.)	(V.)	Disc	Upper	Lower	Cap	(° C.)
0·807	4·96	1·733	1·593	1·205	1·066	16·82

Thermocouple temperatures (° C.)

56·21 53·15 44·53 41·41

Positions of thermocouples (distance from base, cm.)

1·911 1·524 0·322 0·00

Heat input.

Current, 0·807 A., e.m.f. at case terminals, 4·96 V.

Heat input to coil, 0·947 cal./sec.

Heat-loss along thermocouples, 0·002 cal./sec. when $V = 14{\cdot}80°$ C.

Heat emitted from top and sides, 0·074 cal./sec. when $V = 14{\cdot}80°$ C. and $h_0 = 0{\cdot}00018$.

Heat input to specimen, 0·871 cal./sec.

Approximate value of k, $6{\cdot}2 \times 10^{-3}$.

Calculation of α_1 and α_2.

When
$$V = 7{\cdot}43^\circ\ \text{C.}, \qquad h'' = 1{\cdot}35 \times 10^{-4},$$
$$\therefore \quad K = 2{\cdot}18 \times 10^{-2},$$
$$\therefore \quad aK = 5{\cdot}47 \times 10^{-2}.$$

From the curves given in figures 3*a* and 4*a* we have,

$$\alpha_1 a = 0{\cdot}330, \quad \text{so that} \quad \alpha_1 = 0{\cdot}132;$$
$$\alpha_2 a = 3{\cdot}85, \quad \text{so that} \quad \alpha_2 = 1{\cdot}53.$$

Equation (3) may be simplified by certain approximations.

$$\frac{H - h_0 S_0 V}{v_1 - v_2}$$
$$= 2\pi ka \frac{\dfrac{1}{K^2+\alpha_1{}^2}\cdot\dfrac{J_1(\alpha_1 a)}{J_0(\alpha_1 a)}\cdot\dfrac{\cosh\alpha_1 b}{\sinh\alpha_1 b} + \dfrac{1}{K^2+\alpha_2{}^2}\cdot\dfrac{J_1(\alpha_1 a)}{J_0(\alpha_2 a)}\cdot\dfrac{\cosh\alpha_2 b}{\sinh\alpha_2 b}}{\dfrac{1}{K^2+\alpha_1{}^2}\cdot\dfrac{1}{J_0(\alpha_1 a)}\cdot\dfrac{\sinh\alpha_1 z_1 - \sinh\alpha_1 z_2}{\sinh\alpha_1 b} + \dfrac{1}{K^2+\alpha_2{}^2}\cdot\dfrac{1}{J_0(\alpha_2 a)}\cdot\dfrac{\sinh\alpha_2 z_1 - \sinh\alpha_2 z_2}{\sinh\alpha_2 b}}$$
$$= 2\pi ka \frac{J_1(\alpha_1 a).\cosh\alpha_1 b + \dfrac{K^2+\alpha_1{}^2}{K^2+\alpha_2{}^2}\cdot\dfrac{J_0(\alpha_1 a)}{J_0(\alpha_2 a)}\cdot\dfrac{\sinh\alpha_1 b}{\sinh\alpha_2 b}\cdot\dfrac{J_1(\alpha_2 a)}{1}\cdot\dfrac{\cosh\alpha_2 b}{1}}{\sinh\alpha_1 z_1 - \sinh\alpha_1 z_2 + \dfrac{K^2+\alpha_1{}^2}{K^2+\alpha_2{}^2}\cdot\dfrac{J_0(\alpha_1 a)}{J_0(\alpha_2 a)}\cdot\dfrac{\sinh\alpha_1 b}{\sinh\alpha_2 b}\cdot\dfrac{(\sinh\alpha_1 z_1 - \sinh\alpha_2 z_2)}{1}}$$

The second terms in both numerator and denominator are small compared with the first term, that in the numerator being about $\frac{1}{40}$ per cent and that in the denominator 2 per cent of their respective first terms. We can, therefore, write

$$J_0(\alpha_1 a)/J_0(\alpha_2 a) = -2{\cdot}4,$$

since $J_0(\alpha_1 a)$ is always nearly 0·97 and $J_0(\alpha_2 a) = -0{\cdot}4$. The second term in the numerator is negligible.

That in the denominator may be written

$$\frac{\alpha_1{}^2}{\alpha_2{}^2}(-2{\cdot}4)\frac{\sinh\alpha_1 b}{\sinh\alpha_2 b}(\sinh\alpha_2 z_1 - \sinh\alpha_2 z_2).$$

We have
$$J_1(\alpha_1 a) = \tfrac{1}{2}\alpha_1 a\left\{1 - \frac{1}{2}\left(\frac{\alpha_1 a}{2}\right)^2\right\};$$

$$\therefore \frac{H - h_0 S_0 V}{v_1 - v_2}$$
$$= \pi a^2 k\alpha_1 \frac{\left\{1 - \dfrac{1}{2}\left(\dfrac{\alpha_1 a}{2}\right)^2\right\}\cosh\alpha_1 b}{\left\{\sinh\alpha_1 z_1 - \sinh\alpha_1 z_2 - 2{\cdot}4\left(\dfrac{\alpha_1}{\alpha_2}\right)^2\cdot\dfrac{\sinh\alpha_1 b}{\sinh\alpha_2 b}.(\sinh\alpha_2 z_1 - \sinh\alpha_2 z_2)\right\}}.$$

This is the equation used for the determination of.*k*.

Proceeding with the calculation for specimen no. 3, we have that

$$\frac{H - h_0 S_0 V}{v_1 - v_2} = \frac{\pi.2{\cdot}51^2.k.0{\cdot}132\{1 - 0{\cdot}014\}\,1{\cdot}032}{\{0{\cdot}202 - 0{\cdot}042 - 0{\cdot}002\}},$$

whence $k = 6{\cdot}0 \times 10^{-3}$ cal./cm.-sec.-deg.

§8. REVIEW OF RESULTS

The accuracy of the method is chiefly dependent upon the measurement of the distance apart of the couples in the mica holder. In practice the setting up was not considered accurate enough if, when a travelling microscope was moved along the length of the wire parallel to the long edge of the holder, the point of intersection of the cross wires moved off the width of the thermocouple wire. The holders used fulfilled this condition, and as the diameter of the wire was 0·019 cm. the error in distance apart of the couples can be considered to have a maximum of about 0·01 cm. As the distance between the couples was usually about 1·1 to 1·2 cm. one can say that an error of less than 1 per cent is involved on account of the setting up. The final results can, therefore, be considered to be accurate to within 1 per cent.

The method has, of course, the advantage that the error due to the difference of temperature set up in the glycerine layer maintaining thermal contact between the hot and cold plates and the specimen is eliminated.

The rocks used were gabbro, granite, quartz-schist and recrystallized sandstone. The sources were as follows:

Gabbro: from Sligachan, Skye.

Granite: taken at a depth of 270 ft. from the surface at the Newmay Quarry, Aberdeenshire.

Quartz-schist: from Moine, Sutherland.

Recrystallized sandstone: Lower Permian, The Old Quarry, Penrith, Cumberland.

In the case of sandstone a different treatment had to be adopted in the fixing of the mica couple-holder in the specimen, as the sandstone was permeable to the glycerine. Fairly thick shellac varnish was used in place of the glycerine.

The values of the thermal conductivities found with the apparatus are given in the table.

Specimen	Current (A.)	E.M.F. (V.)	Thermocouple readings (mV.)				Cold-junction temperature (° C.)	Density (gm./cm³)	Distances from base (cm.)				Mean temperature of specimen (° C)	*k*
			Disc	Upper	Lower	Cap			Disc	Upper	Lower	Cap		
Gabbro	0·600	3·71	1·049	0·951	0·765	0·688	16·18	3·10	1·91	1·41	0·34	0·00	36·2	0·006
	0·818	5·00	1·793	1·615	1·263	1·115	17·10						49·9	0·005
Granite	0·607	3·69	0·922	0·860	0·700	0·635	15·54	2·58	1·91	1·52	0·32	0·00	33·7	0·008
	0·813	4·99	1·633	1·515	1·217	1·093	15·72						47·0	0·008
Quartz-schist	0·605	3·73	0·883	0·828	0·703	0·650	16·42	2·58	1·91	1·41	0·34	0·00	34·2	0·009
	0·798	4·98	1·410	1·312	1·092	0·996	15·96						43·6	0·009
Sandstone, recrystallized	0·608	3·70	0·978	0·912	0·802	0·723	16·30	2·40	1·91	1·49	0·41	0·00	36·5	0·011
	0·793	4·86	1·509	1·382	1·200	1·056	16·86						46·6	0·011

Comparison with the results obtained by other observers is rather difficult. Widely differing values have been observed for specimens of the same name but which may vary considerably in their composition.

Gabbro was used by Tadakora*. He found the conductivities of horneblende gabbro taken from two provinces in Japan. For a specimen from the Province of Chikuzen the value was 0·0072 while from the Province of Awadi the value was 0·0043, both taken at room temperatures.

Granite was used by Poole† and he gives a value of 6×10^{-3} The present values are much higher, but this is probably due to difference in composition. The amount of quartz, which probably governs the conductivity by both the quantity present and its orientation in the specimen, can, in granite, vary by from 20 per cent to 50 per cent. Poole does not state the source of his specimen.

Quartz-schist is a "sheared quartzite." In this, the quartzite has been crushed by folding movements and the quartz consists of small crystalline fragments of irregular shape with interlocking margins. Some white mica is also contained in crystalline flakes. One might, therefore, expect lower values than those obtained for quartzite. Ensor‡ gives the thermal conductivity of quartzite at 0° C. as 0·0149, which agrees with this expectation.

Previous values for sandstone are considerably lower than the values found, being about 3×10^{-3} at air temperatures. The specimen used in this work is of recrystallized sandstone. The *Encyclopaedia Britannica* states in the section on quartzites that "where sandstones are altered by intrusive rocks they are often converted into pure quartzite, the heat evidently occasioning the deposit of interstitial quartz." Recrystallized sandstone undergoes such forces in its formation, and it is interesting to note that the values of the thermal conductivity observed are of the same order as those for quartzite.

The directions of the variations in the conductivities at the different temperatures agree with those found by previous observers. On account of the limited range no value of a temperature coefficient of thermal conductivity can be given.

§9. ACKNOWLEDGMENT

In conclusion, the author would like to express his thanks to Prof. C. H. Lees, F.R.S., for his suggestions and encouragement throughout the course of this work.

---

* *Science Reports of Tôhoku University*, **10**, 339 (1921).

† *Phil. Mag.* **27**, 82 (1914).

‡ *Proc. Phys. Soc.* **43**, 590 (1931).

536.21

TABLES TO FACILITATE THE CALCULATION OF THE TEMPERATURE-DISTRIBUTION IN A CYLINDER

By H. A. NANCARROW, M.Sc., A.Inst.P., Research Student, East London College

Communicated by Dr Allan Ferguson, November 28, 1932. Read March 17, 1933.

ABSTRACT. The temperature-distribution, in the case of a cylinder heated at its top surface and whose convex surface is exposed to air at the same temperature as that of the base of the cylinder, has been considered by Byerley. The present paper gives curves and a table which can be used for finding constants occurring in the expression for the temperature-distribution.

The cases in which the temperature-distribution in a circular cylinder symmetrically heated may be expressed in terms of Bessel functions may be classified, in accordance with Byerley's* suggestions, as follows.

a, b — r

(*a*) The convex surface and base of a cylinder of radius a and length b are kept at zero temperature, and the temperature at each point of the top surface is a given function of the distance r of the point from the centre of the surface. (*b*) The base is kept at zero temperature and the convex surface is impervious to heat, the top surface being as in (*a*). (*c*) The base is kept at zero temperature and the convex surface of the cylinder is exposed to a gas at zero temperature, the top surface being as in (*a*).

The solution of each of these problems is given by

$$\mu = A_1 \frac{\sinh(\mu_1 z)}{\sinh(\mu_1 b)} \cdot J_0(\mu_1 r) + A_2 \frac{\sinh(\mu_2 z)}{\sinh(\mu_2 b)} \cdot J_0(\mu_2 r) + \ldots.$$

z — $A_1, A_2, \ldots$ — $\mu_1, \mu_2, \ldots$

Where J_0 is the Bessel function of zero order, z the height of a point above the base, A_1, A_2, ... constants to be determined by the distribution of temperature over the upper surface, and μ_1, μ_2, ... are in each case the roots of an equation, namely

for (*a*) $$J_0(\mu a) = 0,$$

for (*b*) $$J_1(\mu a) = 0,$$

for (*c*) $$k\mu a J_1(\mu a) - ah J_0(\mu a) = 0,$$

h, k

where h is the emissivity of the surface and k is the thermal conductivity of the material of the cylinder.

---

* W. E. Byerley, *Fourier Series and Spherical Harmonics*, p. 226 (1902).

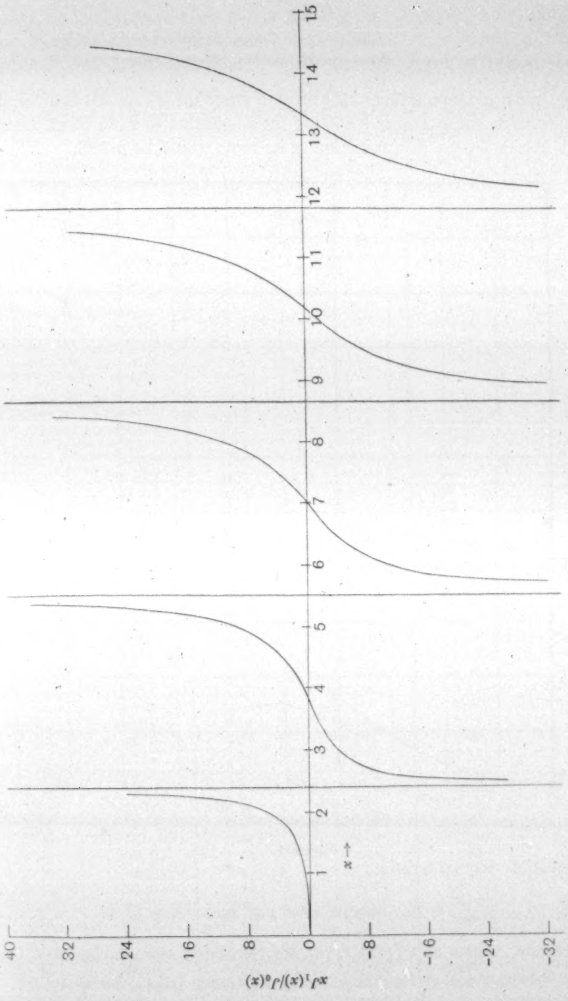

$x \rightarrow$
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
40
32
24
16
8
0
-8
-16
-24
-32
$xJ_1(x)/J_0(x)$

Figure 1.

The roots of (*a*) and (*b*) have been tabulated*, and the lower values are reproduced in table 1.

Table 1.

Roots of $J_0(x) = 0$	2·405, 5·520, 8·654, 11·792, 14·931, 18·071, 21·212
Roots of $J_1(x) = 0$	3·832, 7·016, 10·173, 13·324, 16·471, 19·616, 22·760

There appear to be no tables of the roots of equation (*c*). As this case frequently occurs in practice, the author is following the suggestion of Prof. C. H. Lees, that tables and curves for the determination of its roots would be useful.

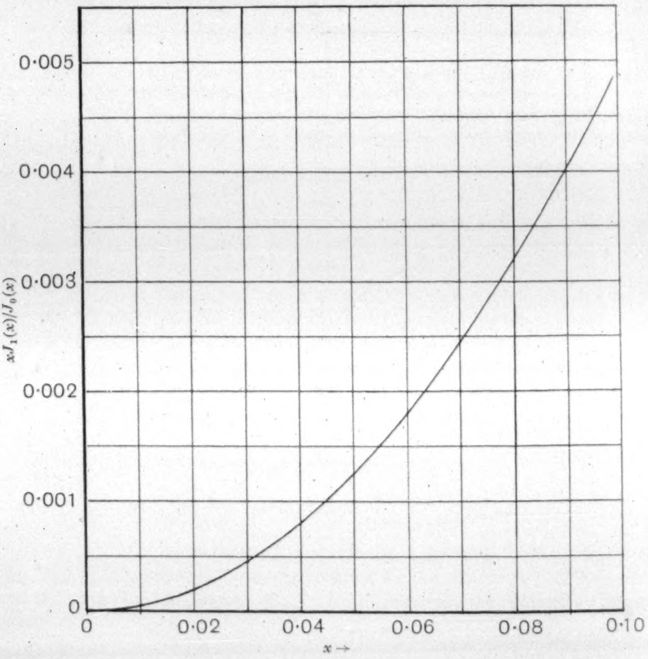


Figure 2.

The equation may be written

x, K

$$\frac{xJ_1(x)}{J_0(x)} = K, \quad \text{where} \quad x = \mu a \quad \text{and} \quad K = ah/k.$$

If, therefore, values of $xJ_1(x)/J_0(x)$ are calculated from tables of $J_1(x)$ and

---

[*] G. N. Watson, *Theory of Bessel Functions*, p. 666 (1922); Jahnke, *Funktionentafeln*, p. 111 (1909).

$J_0(x)$ and plotted against x; the values of x which make $xJ_1(x)/J_0(x)$ equal to K may be found by interpolation or by inspection of the curves. The values of $xJ_1(x)/J_0(x)$ are given in table 2 over the range $x = 0$ to $x = 15$ at small intervals within the ranges likely to be required in practice.

The values when plotted give the curve shown in figure 1. It is, of course, discontinuous, with breaks occurring at the roots of $J_0(x) = 0$, and crosses the x axis at the roots of $J_1(x) = 0$. Each portion gives a value of μ satisfying the equation. The portions over which small intervals have been taken are shown on an enlarged scale in figures 2, 3, 4, 5, 6 and 7. Figures 3*a* and 4*a* are portions of the curve used in work* with some rock specimens.

Table 2.

x	$\frac{xJ_1(x)}{J_0(x)}$	x	$\frac{xJ_1(x)}{J_0(x)}$	x	$\frac{xJ_1(x)}{J_0(x)}$
0·00	0·00	2·20	11·083	8·00	10·936
·01	·00005	2·4048	∞	8·20	17·310
·02	·00020	2·50	−25·64	8·40	32·890
·03	·00045	2·75	− 7·137	8·6537	∞
·04	·00080	3·00	− 3·911	9·00	−24·442
·05	·00125	3·25	− 2·355	9·25	−13·125
·06	·00180	3·50	− 1·268	9·50	− 7·795
·07	·00245	3·75	− 0·310	9·75	− 4·393
·08	·00320	3·8317	0·000	10·00	− 1·769
·09	·00405	3·85	0·0703	10·1735	0·000
·10	·00501	3·90	0·2644	10·20	0·2705
·15	·0113	3·95	0·4624	10·25	0·7830
·20	·0201	4·00	0·6651	10·30	1·3053
·25	·0315	4·05	0·8738	10·35	1·8305
·30	·0455	4·10	1·0894	10·40	2·3704
·35	·0622	4·15	1·3132	10·60	4·7138
·40	·0816	4·20	1·5464	10·80	7·5563
·45	·1039	4·40	2·6069	11·00	11·360
·50	·1291	4·60	3·9850	11·20	17·167
·55	·1573	4·80	5·9592	11·40	28·111
·60	·1886	5·00	9·2222	11·60	60·314
·65	·2243	5·10	11·967	11·7915	∞
·70	·2614	5·20	16·182	12·00	−56·21
·75	·3031	5·40	45·252	12·25	−24·32
·80	·3487	5·5201	∞	12·50	−14·08
·85	·3984	5·75	−24·06	12·75	− 8·448
·90	·4524	5·85	−16·58	13·00	− 4·418
·95	·5112	6·00	−11·03	13·25	− 0·981
1·00	·5751	6·25	− 6·474	13·3237	0·000
1·05	·6444	6·50	− 3·843	13·35	0·3511
1·10	·7197	6·75	− 1·873	13·40	1·0216
1·15	·8018	7·00	− 0·109	13·45	1·7000
1·20	·8909	7·0156	0·000	13·50	2·3892
1·25	·9882	7·05	0·2421	13·55	3·0937
1·30	1·0944	7·10	0·5971	13·60	3·8160
1·35	1·2117	7·15	0·9577	13·80	6·9886
1·40	1·3385	7·20	1·3257	14·00	10·916
1·45	1·4792	7·25	1·7028	14·20	16·333
1·50	1·6351	7·30	2·0913	14·40	25·022
1·60	1·9976	7·35	2·4935	14·60	42·998
1·80	3·0789	7·40	2·9116	14·80	112·92
2·00	5·2719	7·60	4·8092	14·9309	∞
2·10	7·1627	7·80	7·2910		

---

* See page 447 of this volume.

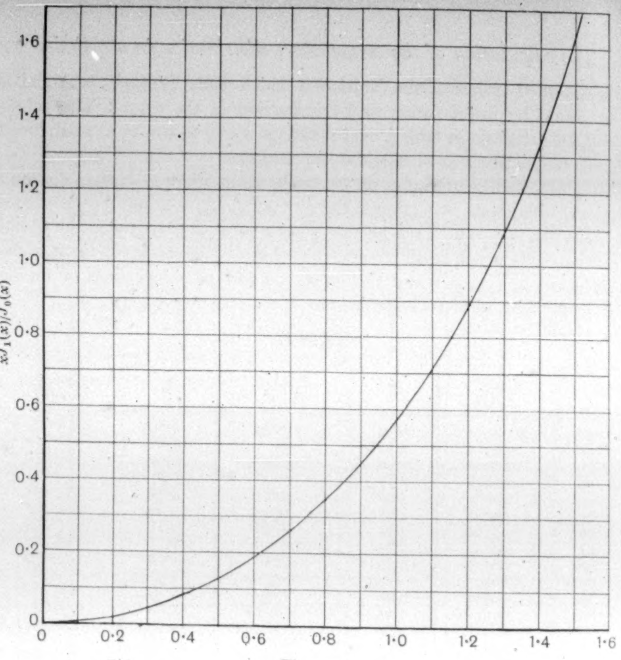


Figure 3.

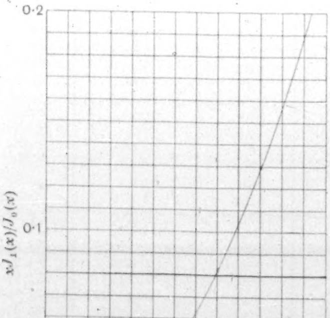


Figure 3 *a*.

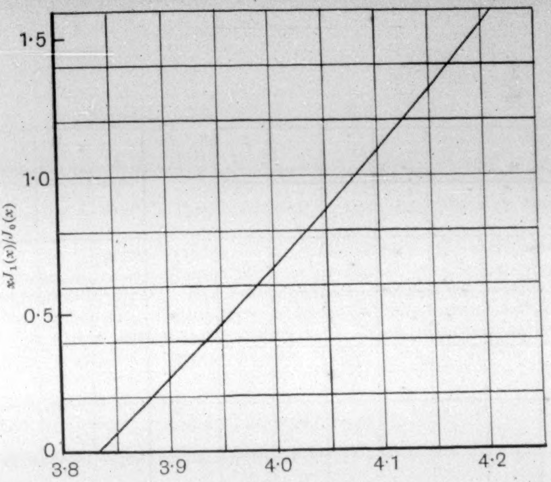


Figure 4.

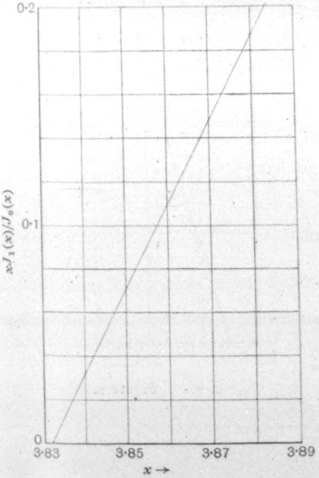


Figure 4*a*.

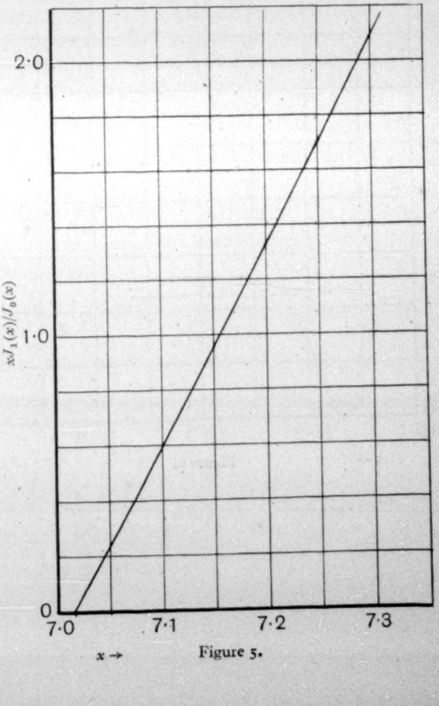


Figure 5.

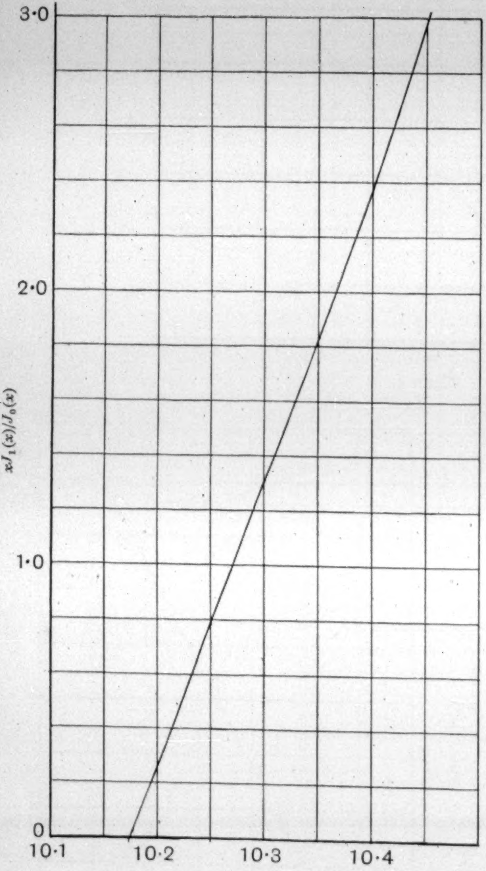


Figure 6.

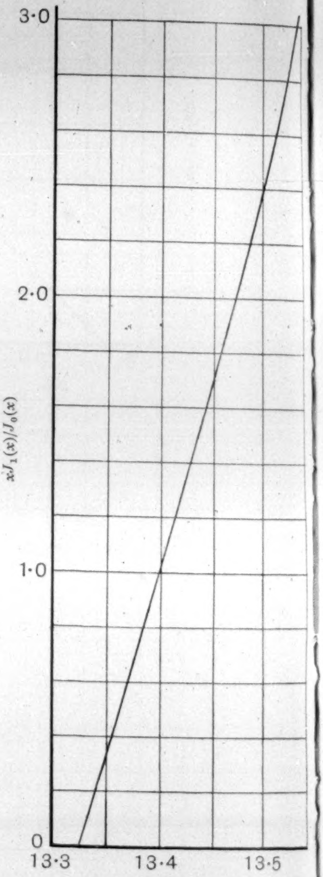


Figure 7.

537.228.3

A NOTE ON THE KERR CELL

By E. E. WRIGHT, B.Sc., Baird Television Limited.

Communicated by Prof. G. Temple, December 31, 1932. *Read March* 17, 1933.

ABSTRACT. The distortion due to the curvature of the (light, voltage) characteristic of a Kerr cell is discussed, and an expression giving the amplitudes of the Fourier components of the light-variation due to a pure alternating potential applied to the cell is obtained. Sets of curves showing the variation of percentage of second and third harmonic with bias and amplitude of the applied alternating potential are given. The working conditions for minimum distortion obtained from these curves agree with those used in practice.

§ 1. INTRODUCTION

The equation of the (light, voltage) characteristic of a Kerr cell* is

$$L = \sin^2 \left\{ \frac{\pi}{2} \left(\frac{e}{V} \right)^2 \right\} \qquad \text{......(1)},$$

where L is the intensity of the light passed by the cell, e the potential applied to the cell, and V the potential at which L is first a maximum. V is a constant for the cell. L, e V

It is obvious from this equation that the light-variations are not proportional to the variations of the applied voltage, although by working on a suitable part of the characteristic and keeping the range of variation of e small the changes in L may be made nearly proportional to the changes in e.

It is the object of this note to investigate this distortion due to the curvature of the characteristic.

§ 2. THEORY

If a pure alternating potential $a \cos \omega t$ superimposed on a steady biasing potential b is applied to the cell, the light-intensity is given by a, ω, t b

$$L = \sin^2 \left\{ \frac{\pi}{2} \left(\frac{b + a \cos \omega t}{V} \right)^2 \right\} \qquad \text{......(2)}.$$

Now L is clearly an even function of time, hence

$$L = A_0 + \sum_{n=1}^{\infty} A_n \cos n\omega t \qquad \text{......(3)}, \qquad n$$

where

$$A_0 = \frac{\omega}{\pi} \int_0^{\pi/\omega} \sin^2 \left\{ \frac{\pi}{2} \left(\frac{b + a \cos \omega t}{V} \right)^2 \right\} dt \qquad \text{......(4)}, \qquad A_0$$

and

$$A_n = \frac{2\omega}{\pi} \int_0^{\pi/\omega} \sin^2 \left\{ \frac{\pi}{2} \left(\frac{b + a \cos \omega t}{V} \right)^2 \right\} \cos n\omega t \, . \, dt \qquad \text{......(5)}. \qquad A_n$$

---

* W. D. Wright, *Proc. Phys. Soc.* **44**, 325 (1932).

The magnitudes of A_1, A_2, A_3 ... determine the nature and extent of the distortion and in particular the expression $100A_2/A_1$ (called "the percentage of second harmonic") is a convenient measure of the distortion. Thus in sound-recording it is usually reckoned that 5 per cent of second harmonic is the maximum distortion tolerable.

Now equation (5) may be written

$$A_n = \frac{1}{\pi}\int_{\pi}^{0} \cos(\alpha + \beta\cos\phi + \gamma\cos 2\phi)\cos n\phi\,.\,d\phi \qquad \text{......(6)},$$

ϕ, α where

β, γ

$$\left.\begin{aligned} \phi &= \omega t \qquad & \alpha &= (b^2 + \tfrac{1}{2}a^2)\,\pi/V^2 \\ \beta &= 2ab\pi/V^2 \text{ and} & \gamma &= a^2\pi/2V^2 \end{aligned}\right\} \qquad \text{......(7)}.$$

It can easily be proved that*

$$\exp\{\tfrac{1}{2}x\,(y - y^{-1})\} = \sum_{m=-\infty}^{+\infty} y^m J_m(x) \qquad \text{......(8)},$$

J_m where $J_m(x)$ is a Bessel coefficient of order m. So that putting $y = i\exp(i\theta)$ and using the relation†

$$J_{-m}(x) = (-1)^m J_m(x) \qquad \text{......(9)},$$

we obtain

$$\exp(ix\cos\theta) = J_0(x) + 2\sum_{m=1}^{\infty} i^m J_m(x)\cos m\theta \qquad \text{......(10)}.$$

Therefore A_n is the real part of

μ, λ

$$\frac{\exp(i\alpha)}{\pi}\int_{\pi}^{0}\left\{J_0(\beta) + 2\sum_{\mu=1}^{\infty} i^{\mu} J_{\mu}(\beta)\cos\mu\phi\right\}\left\{J_0(\gamma) + 2\sum_{\lambda=1}^{\infty} i^{\lambda} J_{\lambda}(\gamma)\cos 2\lambda\phi\right\}\cos n\phi\,.\,d\phi$$

$$\begin{aligned} &= \exp(i\alpha)\left[J_0(\beta)\,J_0(\gamma)\int_{\pi}^{0}\frac{1}{\pi}\cos n\phi\,.\,d\phi\right. \\ &\quad + J_0(\gamma)\sum_{\mu=1}^{\infty} i^{\mu} J_{\mu}(\beta)\int_{\pi}^{0}\frac{2}{\pi}\cos\mu\phi\cos n\phi\,.\,d\phi \\ &\quad + J_0(\beta)\sum_{\lambda=1}^{\infty} i^{\lambda} J_{\lambda}(\gamma)\int_{\pi}^{0}\frac{2}{\pi}\cos 2\lambda\phi\cos n\phi\,.\,d\phi \\ &\quad \left. + \sum_{\mu=1}^{\infty}\sum_{\lambda=1}^{\infty} i^{\mu+\lambda} J_{\mu}(\beta)\,J_{\lambda}(\gamma)\int_{\pi}^{0}\frac{4}{\pi}\cos 2\lambda\phi\cos\mu\phi\cos n\phi\,.\,d\phi\right] \qquad \text{......(11)}. \end{aligned}$$

Of the integrals in this expression the first is zero; the second is (-1) when $\mu = n$, otherwise it is zero; the third is (-1) when $2\lambda = n$, otherwise it is zero; and the last is (-1) each time any of the following conditions are fulfilled:

$$2\lambda + \mu = n, \quad 2\lambda + n = \mu \ \text{ and } \ \mu + n = 2\lambda.$$

Otherwise it is zero.

With these conditions it is a simple matter to pick out an expression for A_n for any particular value of n.

---

* Watson, *Theory of Bessel Functions*, p. 14.

† *Ibid.* p. 15.

Thus:

$$\begin{aligned} A_1 = {} & \cos\alpha\,[J_1(\gamma)\,\{J_1(\beta) - J_3(\beta)\} - J_3(\gamma)\,\{J_5(\beta) - J_7(\beta)\} \\ & + J_5(\gamma)\,\{J_9(\beta) - J_{11}(\beta)\}\,\ldots] \\ & + \sin\alpha\,[J_0(\gamma)\,J_1(\beta) + J_2(\gamma)\,\{J_3(\beta) - J_5(\beta)\} - J_4(\gamma)\,\{J_7(\beta) - J_9(\beta)\}\,\ldots], \end{aligned} \tag{A_1}$$

$$\begin{aligned} A_2 = {} & \cos\alpha\,[J_0(\gamma)\,J_2(\beta) - J_2(\gamma)\,\{J_2(\beta) + J_6(\beta)\} + J_4(\gamma)\,\{J_6(\beta) + J_{10}(\beta)\}\,\ldots] \\ & + \sin\alpha\,[J_1(\gamma)\,\{J_0(\beta) + J_4(\beta)\} - J_3(\gamma)\,\{J_4(\beta) + J_8(\beta)\} \\ & + J_5(\gamma)\,\{J_8(\beta) + J_{12}(\beta)\}\,\ldots], \end{aligned} \tag{A_2}$$

$$\begin{aligned} A_3 = {} & \cos\alpha\,[J_1(\gamma)\,\{J_1(\beta) + J_5(\beta)\} + J_3(\gamma)\,\{J_3(\beta) - J_9(\beta)\} \\ & - J_5(\gamma)\,\{J_7(\beta) - J_{13}(\beta)\}\,\ldots] \\ & - \sin\alpha\,[J_0(\gamma)\,J_3(\beta) + J_2(\gamma)\,\{J_1(\beta) - J_7(\beta)\} - J_4(\gamma)\,\{J_5(\beta) - J_{11}(\beta)\} + \ldots], \end{aligned} \tag{A_3}$$

and so on.

Now in any practical use of these series the maximum value of γ is about 0·25 and that of β is about 2, so that the series converge very rapidly, two terms of each being sufficient to give their sums to about four figures. Bessel coefficients are tabulated at the end of Watson's *Theory of Bessel Functions* and have been plotted by Hague.*

The value of A_0 is comparatively unimportant, but it may be found by an analysis very similar to the above.

§ 3. RESULTS

Figures 1 and 2 show the percentage of second harmonic for various values of the amplitude of the applied voltage and the bias. In considering these curves it must be remembered that the percentage of second harmonic is not the only factor to be considered; for if the cell is used over a range in which the characteristic is

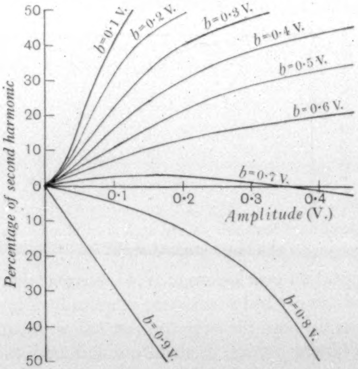


Figure 1. Percentage of second harmonic plotted against amplitude of the applied voltage at various bias voltages.

---

* *Proc. Phys. Soc.* **29**, 211 (1917).

nearly symmetrical about the centre point the even harmonics will be small compared with the odd harmonics. For this reason an additional curve, figure 3, showing the relation between the percentage of third harmonic and the amplitude of the applied voltage when the biasing voltage is 0·7 is given.

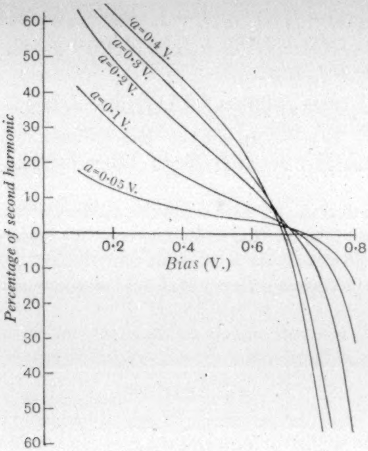


Fig. 2. Percentage of second harmonic plotted against bias at various values of the amplitude of the applied voltage.

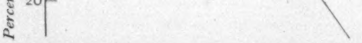


Fig. 3. Percentage of third harmonic plotted against amplitude of the applied voltage at a bias voltage of 0·7 V.

These curves support the conclusions of W. D. Wright* that for sound-recording a biasing voltage of about 0·7 and a maximum amplitude of just over 0·1 V. should be used. In television the need for large contrast has to be satisfied at the price of distortion, so that a biasing voltage of about 0·6 and amplitudes up to 0·4 V. are used, giving about 20 per cent of second harmonic and 9 per cent of third harmonic. Fortunately the eye is not very sensitive to this shade-distortion.

---

* *Loc. cit.*

DISCUSSION

Prof. A. O. RANKINE referred to the author's statement on page 472 that W. D. Wright had found the optimum biasing voltage to be 0·7, and asked whether this result was obtained by trial, or by calculation from equation (1).

Dr W. D. WRIGHT. I am afraid I cannot claim the credit that has been attributed to me for the values of the biasing and modulating voltages used in sound-recording. They originated in a paper by Zworykin, Lynn and Hanna* to which I referred in my paper on the Kerr cell and they were based on the same criterion as that used by the author of the present paper, namely that not more than 5 per cent of second harmonic is tolerable. The agreement found is therefore to be expected.

AUTHOR'S reply. I imagine that the conditions under discussion were initially arrived at merely by noticing that the characteristic curve is substantially straight between 0·6 V. and 0·8 V.

* *Trans. Soc. Motion Picture Engineers*, **12**, 748 (1928).

535.42

AN EXPERIMENT BEARING ON TALBOT'S BANDS

By the late A. CHRISTOPHER G. BEACH, B.Sc., A.Inst.P.,
Chelsea Polytechnic

Received November 19, 1931*. *Read in title March* 17, 1933.

ABSTRACT. The author discusses the form of diffraction pattern observed in a spectroscope when a point of light is produced on the slit of the collimator, and an aperture in which the upper or lower half is covered with a retarding plate is between the collimator and telescope. He uses the bands so produced as a means to explain Talbot's bands, and shows how the method helps to find the best aperture-width to exhibit them. A description of the experimental methods and photographs of the effect are given.

§ 1. INTRODUCTION

Talbot's bands are produced in a spectroscope if white light is sent through it and half the beam is made to pass through a retarding plate of some transparent material, provided that the edge of the retarding plate is parallel to the slit and that the plate is inserted from the red side of the spectrum if placed between the collimator lens and the telescope objective, or from the other side if placed at the eyepiece. In order to get sharp bands there is a definite relation between the angular dispersion of the prism, the rate of change of phase-retardation produced by the plate, and the width of beam. The bands were discovered by Fox Talbot in 1837 and were explained by Airy, and later by Stokes. These two treatments are mathematical and are based on Fourier's analysis. In 1904 Schuster suggested an explanation based on the pulse theory of white light and, as a result, Talbot's bands have been considered to prove the pulse theory. Another method of explanation, which does not require the pulse theory, is that given by A. W. Porter†, who compares the arrangement to a two-aperture echelon grating.

During the summer of 1928 the author carried out some experiments the result of which also was to show that the pulse theory was not necessary to explain these bands. The method adopted, and shown in figure 2, was to focus the image of an electric-lamp filament L on the slit of a spectroscope and so to produce a point source of light at the focus of the collimator lens. When this point is viewed through the spectroscope the continuous spectrum is seen reduced to a horizontal line. If now the retarding plate F and aperture are placed as for Talbot's bands but rotated in their plane through 90°, a diffraction pattern is seen of oblique lines crossing the horizontal axis of symmetry and these oblique lines are cut into short lengths by dark bands nearly parallel to the axis.

---

* The Council regret the delay in publication of this paper, occasioned by the sudden and lamented death of the author. The paper in its original form was part of a thesis for B.Sc. by research.

† Preston, *Theory of Light*. Edited by A. W. Porter, p. 320 (5th edition).

Any point on this pattern can be considered as being produced by two displacements, one in the plane of the deviation, due to the spectroscope, and the other perpendicular to this, due to the diffraction pattern. The rate of change of these displacements with change of wave-length depends in the first case on the constants of the prism or grating, in the second on the rate of change of phase-retardation produced by the film and on the aperture-width, so that the slope of a line depends on the relative values of these two rates of change. If now the aperture is given such a width that the lines are at 45°, the two rates of change are equal and the aperture is the best to show Talbot's bands.

A series of points can be taken along the axis of symmetry of the spectra which are in the same condition of intensity of illumination. (As will be shown in the theory it is best to choose the points of zero illumination, as the zero-illumination lines are straight.) Let these points be considered as zero-displacement points, then on one side of each there is positive displacement for both axes and on the other there is negative displacement. Now turn the aperture and film through 90° in the plane of the film. This brings both sets of displacements into one axis. If the film is turned one way the displacements oppose each other and therefore sum to zero. This gives Talbot's bands. If the film is turned the other way they supplement each other and no bands can be produced.

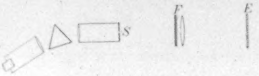


Figure 1.

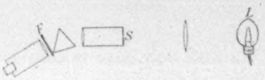


Figure 2.

On looking at the literature on the subject, the author found that N. K. Sethi had published in 1920* a description of somewhat similar oblique bands produced by a different optical arrangement. His method, figure 1, was to project the image of a slit *E* on to the slit of the spectroscope and then to place the aperture and retarding plate *F* close to the projection lens. The resulting effect at the slit of the spectroscope was analysed by the spectroscope and gave a similar diffraction pattern. The author has continued his experiments and now publishes them because his arrangement has advantages over Sethi's in that the development from the oblique bands to Talbot's bands can be carried out in a more logical and straightforward manner and, further, the method gives a means of determining quickly the best aperture-width.

§ 2. THEORY

In the mathematical discussion which follows the theory of the oblique bands is first considered, as these bands have an interest of their own. The results are then developed to show their bearing on Talbot's bands. The discussion depends on the theory of a rectangular aperture, and the usual textbook proofs are assumed but are developed further or by different methods where such a course is helpful.

* *Phys. Rev.* **16**, 519–525 (1920).

In each method an expression is obtained for the amplitude of the oscillations in a given direction. To change this expression into intensity it must be squared.

λ Let monochromatic light of wave-length λ pass normally through a rectangular
e, e' aperture of sides e, e', in the XY plane, figure 4.

a, θ In order to find the amplitude a of the oscillations in a direction OP let θ be the
θ' angle which OP makes with its projection on the YZ plane and θ' be the angle which
this projection makes with the OZ axis. Then by the usual methods

$$a = A\frac{\sin\Phi}{\Phi}\cdot\frac{\sin\Phi'}{\Phi'} \qquad \text{......(1)},$$

Φ, Φ' where Φ, Φ' are phase differences and are of the form

$$2\Phi = \frac{2\pi e\sin\theta}{\lambda} \qquad \text{......(2)}.$$

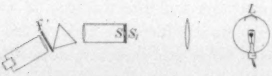


Figure 3.

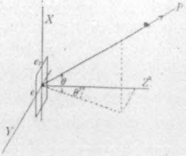


Figure 4.

We shall only have to consider the variation in amplitude and intensity with variation of direction in one plane, say the XZ plane, and therefore Φ' and θ' can be considered fixed while Φ and θ are variables. If, in addition, our aperture is a long narrow aperture or slit and our plane is perpendicular to this and passes through its centre,

$$a = A\frac{\sin\Phi}{\Phi} \qquad \text{......(3)},$$

A where A is the amplitude in the direction OZ.

The variation of a with Φ can be shown to pass through maximum, zero and minimum values by differentiating equation (3), but it is of interest to discuss this by means of a vector diagram, as such a diagram can be used to develop the theory of a long aperture in which half the aperture is covered by a transparent plate with its edge parallel to the long side of the aperture. Let the XZ plane cut the centre of the aperture. To find the effect in a direction OP in this plane, divide up the width e of the aperture into strip elements parallel to the Y axis. The amplitude of the disturbance in the given direction is the same for each strip, but the phase changes gradually in passing from one edge of the aperture to the other. Let this change be 2Φ. Then

$$2\Phi = \frac{2\pi e\sin\theta}{\lambda} \qquad \text{......(2)}.$$

To add these disturbances by means of a vector diagram, let a vector of magnitude
m m represent the disturbances received from each strip of the aperture and be drawn

as a radius of m units within an angle AOB equal to 2Φ in a circle with centre O, as in figure 5. Let N be the total number of vectors. Then

$$Nm = A \qquad \text{......(4)},$$ N

and A is the effect in a direction P if all the disturbances arrive in the same phase.

If the vectors are not in the same phase but are spread over an angle 2Φ we combine the effects in pairs from two equal angles $d\phi$ at equal angles ϕ but on opposite sides of the bisector of AOB.

The number of vectors n within the angle $d\phi$ is $Nd\phi/2\Phi$ and their combined effect is $Nm\,d\phi/2\Phi$. The resultant along OR of the vectors contained in each pair of angles $d\phi$ is n

$$\frac{2Nm}{2\Phi}\cos\phi\,d\phi,$$

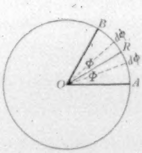


Figure 5.

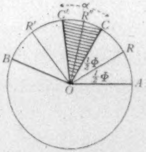


Figure 6.

and integrating over the range 2Φ we have

$$a = \int_0^{\Phi} \frac{Nm}{\Phi}\cos\phi\,d\phi,$$

$$a = \frac{Nm\sin\Phi}{\Phi},$$

or, writing A for Nm,

$$a = \frac{A\sin\Phi}{\Phi} \qquad \text{......(5)}.$$

It will be seen that Nm/Φ gets smaller at each cycle and therefore the maxima get smaller, and also that the resultant is zero each time OB completes a revolution—i.e. when $\Phi = n_1\pi$, where n_1 has the values 1, 2, 3, etc.

To apply this method to the case where half the aperture is covered by a transparent plate, let the plate increase the optical path by δ. If this increased path is expressed in wave-lengths of the particular light the path is increased by δ/λ wave-lengths, which may not be a whole number. In general there is thus a phase-difference of α between the light which just misses the edge and that which just passes through the plate. δ α

Let figure 6 represent this. Each half of the vector diagram of the aperture has a maximum resultant of $\frac{1}{2}A$ when $\Phi = 0$, but the resultants are separated by an angle α. The final resultant is found by projecting R and R' on to a line which bisects the angle between them. This gives

$$a = 2\left(\tfrac{1}{2}A\cos\tfrac{1}{2}\alpha\right),$$

and in general when Φ is not zero the angle between the resultants is $\alpha + \Phi$, and then

$$a = 2\left(\frac{A}{2} \cdot \frac{\sin \frac{1}{2}\Phi}{\frac{1}{2}\Phi} \cos \frac{\alpha + \Phi}{2}\right) \qquad \ldots\ldots(6).$$

It will be seen that the resultant is zero in the vector diagram when the two component resultants oppose each other: i.e.

$$ROR' = \alpha + \Phi = \pi,$$

or when each of these component resultants is zero: i.e. when

$$AOC = 2\pi,\ C'OB = 2\pi.$$

In the first case

$$\cos \tfrac{1}{2}(\alpha + \Phi) = 0,$$

and in the second

$$\frac{\sin \frac{1}{2}\Phi}{\frac{1}{2}\Phi} = 0.$$

If the retardation is such that there is no phase-difference between the two halves, then the effect is the same as if no plate were present. If on the other hand $\alpha = \pi$, then when $\Phi = 0$ the amplitude is zero but it gradually increases with increasing Φ.

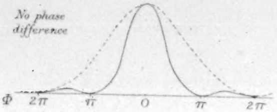


Figure 7.

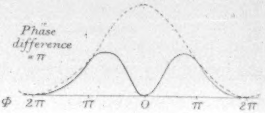


Figure 8.

These two conditions are shown in figures 7 and 8, where the intensity is plotted against the angle Φ. Figure 7 shows the condition when there is no phase-difference and figure 8 when there is a phase-difference of π between the two beams. The dotted curves are intensity curves for an aperture equal to half the given aperture, but the intensity ordinates are increased so as to make comparison easier. It will be seen that the maxima in figure 8 occur on each side between $\frac{1}{2}\pi$ and π. The positions in which they lie are found by differentiating equation (6) and then equating to zero. It is generally shown that $\Phi = \tan \Phi$ gives the position of the maxima for a simple aperture as in figure 7. Applying this method for the other case, figure 8, we have $\Phi = \tan \frac{1}{2}\Phi$.

In considering the case of white light, in order to make the discussion more precise let us suppose that white light radiates from a point and is then made parallel by a lens, after which it passes through a narrow horizontal aperture and is then spread out by a prism into a horizontal spectrum. This spectrum can be brought to a focus in some plane by a lens. There will be a diffraction pattern symmetrically arranged above and below a horizontal narrow continuous spectrum which stretches from red to violet; this line corresponds to the condition that $\theta = 0$. As there is a simple aperture the diffraction pattern consists of light and dark bands nearly parallel to the central band but slowly converging in the direction of the violet end, because if λ is decreasing in equation (2) $\sin\theta$ must also decrease for any given value of Φ.

If now half the aperture be covered by a plate or film of thickness S_1 placed S_1 with its edge horizontal, there is a difference of optical path between the two halves of the beam amounting to $S_1(\mu - 1)$; and expressing this difference in wave-lengths as before we have

$$N_1 = S_1(\mu - 1)/\lambda \qquad \text{......(7).}$$ N_1

In this equation S_1 is a constant, $(\mu - 1)$ increases about 4 per cent in passing along the spectrum from red to violet, but λ becomes halved in the same range. The result is that the difference in phase passes rapidly through cycles from 0 to 2π as we pass along the spectrum. This is chiefly due to the variation of λ. The result is that the diffraction lines are tilted and cross the axis of symmetry for those wave-lengths for which $\alpha = 0$. In addition, the condition that $\sin \frac{1}{2}\Phi / \frac{1}{2}\Phi = 0$ must be taken into account. It will be seen that this is independent of λ and corresponds to the condition that the angles AOC and C_1OB are each equal to 2π in the vector diagram and therefore have no resultants. This condition gives dark bands corresponding to the 2nd, 4th, etc. bands of the plane aperture, and they run right along the system from end to end.

To apply these arguments to Talbot's bands: let a system of bands as described be produced by inserting a horizontal aperture and plate in a spectroscope as in figure 2. The width of the aperture and the thickness of the plate are so adjusted that the oblique bands are at 45° where they cross the central axis. Let θ be measured from a horizontal plane passing through the aperture, and let ψ be the deviation ψ produced by the spectroscope; then for this condition

$$\frac{d\psi}{d\lambda} = \frac{d\theta}{d\lambda}.$$

Let figure 9 represent the condition about a point $O = \psi$ where a dark line crosses the axis; then any point S' is formed by displacing S through a distance SS' equal to its distance from O and of the same sign. If now the same aperture and plate are inserted as for Talbot's bands, each point S is displaced in the direction of O equal to its distance from O and therefore every point on the oblique line from $-\psi_2$ to $+\psi_2$ is collected at O. If, on the other hand, the aperture and plate are inserted from the wrong side, all the points are displaced further apart over twice the distance from $-\psi_2$ to $+\psi_2$, and no bands are formed.

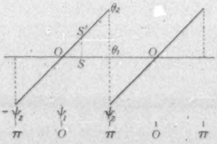


Figure 9.

It will be seen that when the aperture and plate are in position to form Talbot's bands, the width of the beam through the spectroscope is limited to e and the centre of each dark band occurs where $\alpha = \pi$, which is the distance on each side of ψ_1 at which the first minima occur. This fact has been recognized in all the theories of Talbot's bands but is very clearly shown by this method.

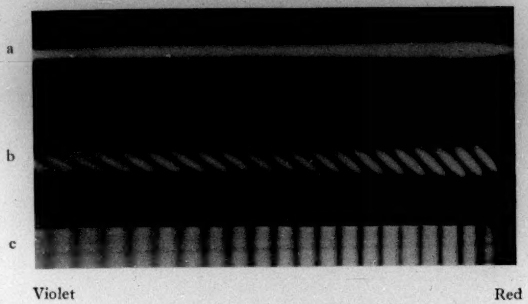
Although any series of repeating points can be taken as the series of origins O, the above argument most closely applies to the displacement and position of minima. As a result of the position of the maxima as shown in figures 7 and 8, the bright bands are not quite straight.

§ 3. EXPERIMENTAL

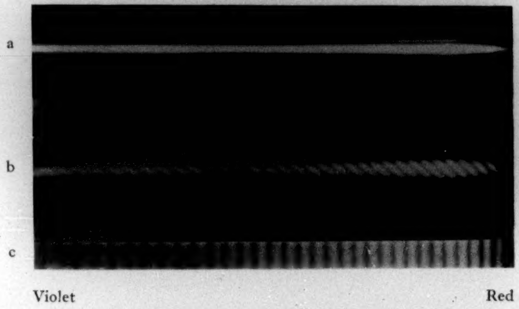
To produce the oblique bands described, and Talbot's bands, the writer used cellulose nitrate films. These films can be prepared of such a range of thicknesses that they give from 10 to 80 bands in the visible spectrum. The bands being broad are more easily seen than when a thicker material, such as a microscope cover-glass, which gives some hundreds of bands is used. To prepare these films cellulose nitrate varnish was diluted until it ran freely and was poured down a piece of plate glass standing almost vertical in a dish. The coat was allowed to dry and another was poured from a different edge. From two to eight coats were poured on in this way. When the last coat was dry the plate was placed in distilled water and the film floated off.

To show these effects visually apparatus was arranged as shown in figure 2. A spectroscope was set up with a glass prism in the position for minimum deviation. A 6-volt lamp L with a V filament having two straight limbs was focussed by an achromatic lens on to the spectroscope slit so that the image of one limb was perpendicular to the slit and crossed its centre. A simple brass slit in which one jaw could be slid out to give any aperture up to 1 cm. was clamped with its slit horizontal and close to the telescope objective. The transparent film or plate F was stuck across an opening in a card, and the card was fastened to the adjustable slit with plasticine, as it was necessary, whenever the aperture-width was altered, to move the film so that its edge should be along the centre of the aperture. Adjustment of the width was now made by trial and error until the bands occurred at 45° at their centre. This can only occur in one region of the spectrum at a time. The brass slit was now removed and measured and a permanent aperture of the same width was cut in thin fibre or card. Used with the same film this aperture gave the best bands in the part of the spectrum where the interference bands were nearest to 45°.

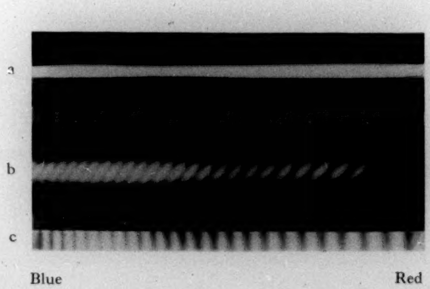
In order to photograph the effects it was found better to use the arrangement shown in figure 3. The slit S of the spectroscope was crossed by a second slit S'. The image of the sphere of a pointolite lamp was brought to a focus on the crossed slits so as to give a point source at the focus of the collimator lens. The adjustments were made as before. The eyepiece of the telescope was removed and the camera was placed in position. The camera consisted of a microscope objective mounted as in a photomicrographic apparatus, the objective taking the place of the telescope


a
b
c
Violet
Red

Prism. Film-thickness, 0·035 mm.; aperture-width, 1·22 mm.


a
b
c
Violet
Red

Prism. Film-thickness, 0·063 mm.; aperture-width, 2·54 mm.


a
b
c
Blue
Red

Grating, 3600 lines to inch; film-thickness, 0·035 mm.; aperture-width, 0·93 mm.

a, uncovered aperture; b, horizontal aperture half-covered with film; c, Talbot's bands.

eyepiece. The advantage of this arrangement is that different magnifications can be obtained by changing the objective. The plate used was Ilford's Fast Soft-gradation Panchromatic plate, stated by the makers to have a speed of 2000 H. and D. A dilute methylene blue solution was used as a filter with the prism in order to reduce the intensity round the yellow part of the spectrum.

Two sets of photographs are shown taken with a 60° crown glass prism and one with a grating of 3600 lines to the inch. In each set is shown: (1) the diffraction effects of a simple horizontal aperture at F; (2) the effect of covering half the aperture with an appropriate film; (3) the Talbot's bands when the aperture is turned to the correct position to show them.

§ 4. ACKNOWLEDGMENTS

The author's thanks are due to Dr Lownds for his interest in this research, and to Miss B. M. Pam, who made the varnish and films.

DISCUSSION

Dr J. R. Milne. A simple and concise explanation of Talbot's Bands was given by the late Mr James Walker of Oxford. It was published in the *Philosophical Magazine* for April 1906, and also in the *Proceedings of the Physical Society*, volume 20.

538.56

DEMONSTRATION

"Experiments with ultra-short electric waves." *Demonstration given on February* 17, 1933, *by* N. L. YATES-FISH, M.A., D.Phil., Assistant-Lecturer in Physics at University College, London.

The transmitter illustrated in figure 1 functions on the Barkhausen-Kurz principle* on a wave-length of 65 cm. The valve-holder projects through a hole in a vertical wooden board, and to the grid and plate sockets is connected a pair of horizontal wires 12 cm. long, forming with the internal leads of the valve an open-ended Lecher-wire system. The ends of these wires are attached to two vertical rods 30 cm. (i.e. nearly half a wave-length) long, which form the radiating elements. In this way the radiation is greatly increased and tends to be concentrated in a horizontal direction. The circuit is given in figure 2, the arrows indicating the distribution of the oscillatory current. The high-frequency chokes at the points where the four leads are attached to the valve-holder have about ten turns each, the two filament leads being twisted together and wound on a single former.

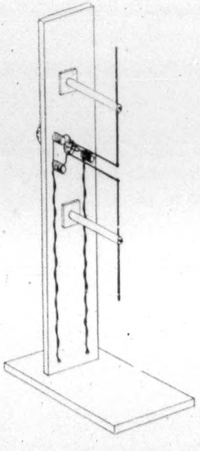


Figure 1.

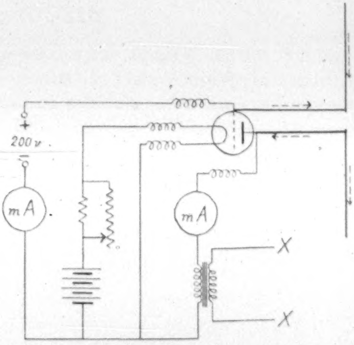


Figure 2.

The valve is a small army transmitting valve of type A T 40 taking a filament current of 1·5 A. at 7·5 V. The filament temperature is controlled by a rheostat of a few ohms' resistance shunted by a piece of resistance wire, this being the only critical adjustment. At the wave-length used the optimum grid-potential is about 200 V. (positive), the current lying between 100 and 200 mA. and the grid attaining a bright red heat. To indicate the setting-in of oscillations a milliammeter reading up to 20 mA. or so is inserted in the plate lead.

---

* See e.g. F. B. Pidduck, *Treatise on Electricity* (second edition), ch. XI; F. W. Chapman, *The Wireless Engineer*, **11**, 108, September 1932.

In order to produce an audible signal the transmitter is modulated by a low-frequency valve oscillator connected to the points *XX* in figure 2. This oscillator can if necessary be dispensed with, as it is found that if a low-frequency choke is connected in series with the plate lead the circuit will howl of its own accord at certain highly critical values of the filament current. Alternatively, unsmoothed direct-current mains can be used to supply the grid-potential.

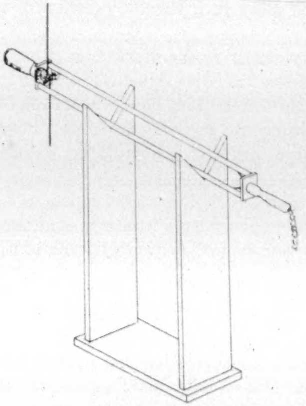


Figure 3.

The receiver, shown in figure 3, consists of an ordinary receiving valve (Osram HL 2) mounted at the end of a pair of wooden rods 80 cm. long and provided with a handle, the four leads being passed along the rods and through a hole drilled along the centre of the handle, thus ensuring a minimum of disturbance of the field around the antenna. Each lead is coiled into a small high-frequency choke of a few turns at the point where it is connected to the valve socket. The antenna wires, each 17 cm. long (the length is not very critical) are attached to the grid socket and one of the filament sockets respectively. The valve is biased as for anode-bend rectification and is coupled by means of a resistance in its anode circuit to an ordinary three-valve low-frequency amplifier and loudspeaker. The receiver can be rested on its wooden stand with the antenna either vertical or horizontal as desired.

The transmitter and receiver are set up several yards apart and as far as possible from all metal pipes, wires, etc. which would introduce stray reflections. Two screens, formed by stretching copper wires parallel to one another and 2 cm. apart across wooden frames 4 ft. square, are used in the experiments. One of these screens placed in the path of the waves with its wires vertical will almost completely cut off the radiation; with the wires horizontal, however, there is no effect, indicating that the waves are plane-polarized. This can also be shown by rotating the receiving antenna into a horizontal position, no signal being then received. If one of the screens is now interposed and rotated in its own plane a feeble signal reappears when the wires are at an angle in the neighbourhood of 45° to the horizontal; the screen is then causing a rotation of the plane of polarization. The reflection of waves can be demonstrated by cutting off the direct radiation with one screen and placing the other in a suitable position to reflect waves on to the receiver.

A very effective experiment is the illustration of the action of the Heaviside layer in producing fading of wireless signals. The layer is represented by a large metal sheet, or one of the screens with its wires vertical, held parallel to the plane containing the transmitting and receiving antennae. Interference takes place between the direct radiation and that reflected from the sheet, and by moving the latter to and fro the variations of intensity due to changes in the effective height of the layer can be simulated.

The existence of diffraction fringes is clearly demonstrated when the receiver is moved from side to side immediately behind one of the screens placed in the path of the waves.

The apparatus was constructed at the suggestion of Prof. E. N. da C. Andrade, who had planned to demonstrate the Heaviside layer by the method just described at his Royal Institution Lectures of November 1932 and required a suitable transmitter for the purpose. I have enjoyed throughout the benefit of frequent consultation with him.

REVIEWS OF BOOKS

Biographical Fragments, by Sir ARTHUR SCHUSTER, F.R.S. Pp. xiii + 268 and 8 plates. (London: Macmillan and Co., 1932.) 10*s*. 6*d*. net.

Readers of this book will be disposed to sympathize certainly with the feelings and possibly with the language of the archaeologist who unearths a few shards which shew they were once parts of a beautiful vase. For the early life of the author the fragments are fortunately fairly numerous, but for the later they are sadly deficient and can only be put together by the help of the indifferent clay provided by proceedings of scientific societies and catalogues of scientific papers.

Sir Arthur Schuster comes of a Jewish business family which a century ago had members in Frankfort-on-Main, Manchester and London. He was born in Frankfort on September 12, 1851. He succeeded when only 5, and still in petticoats, in getting sent to a private school with his elder brother. Here he was at first fairly happy and kept the top of his class, but an illness at 10 made it necessary for him to study under a private tutor in order to enter the gymnasium at 12. This tutor lived with the family for many years and helped Schuster in his mathematics when he left the gymnasium at 16½. An amusing account of the school is given, but he must have found the teaching uninspiring, had no desire to reach the top class, and left without regret. In the meantime Frankfort had been taken by Prussia during the seven weeks' war and the family had Prussian officers and men quartered on them. Anti-Prussian feeling ran high and Schuster's father decided to transfer his business and family to Manchester and to take on British nationality.

As Schuster and his two brothers were to enter the business, they were sent in turn to Geneva to improve their French. Schuster spent a year there and in addition to his French studies attended lectures in history, physics, chemistry, and anatomy, and did astronomical work in the observatory. This period seems to have been one of the happiest of his life and he records that he shed tears as the train left Geneva in May 1870 to take him to Frankfort, where he was to learn banking. The outbreak of the Franco-German war in July found him at Lytham, which had become the seaside resort of the family, and his business career began in the Manchester office of Schuster Brothers. By this time he had set his heart on a scientific career and the uncongenial office work was only partially compensated by attendance at Roscoe's evening classes in chemistry at the Owens College. His mother, who had now lost her sight, was the first to understand how unhappy he was, and it was due to her insight that his father consulted Roscoe, and that Schuster at 20 entered the college for a year to study physics under Balfour Stewart and mathematics under Barker. In a top room of the old Quay Street building he made the observations on the spectrum of nitrogen which formed the subject of his first paper, published by the Royal Society. After a further year at Heidelberg under Kirchhoff he obtained the Ph.D. degree, taking physics as his principal and mathematics and chemistry as his subsidiary subjects. His accounts of life and work in Heidelberg in 1872 are interesting and valuable. The story on p. 219 of the unruffled way in which Kirchhoff, after announcing at his Thursday morning lecture that he would be unable to lecture on Friday morning but would lecture as usual on Monday, used the Friday morning for his wedding and the week end for his honeymoon may have led to the legend of the professor who after setting his class to write an essay "while he attended to a little business," returned before the end of the hour and collected the scripts, having got married in the interval. On his return to Manchester in the summer of 1873 Schuster was appointed demonstrator in the physical laboratory of Owens College, which then consisted of three rooms in the basement of the new building in Oxford Road. The following summer vacation he spent in Weber's somewhat primitive laboratory at Göttingen, and the autumn in Helmholtz's laboratory at Berlin, returning to Hampstead, where his father then lived, at Christmas 1874. He was at first asked to join, and ultimately to take charge of, the Royal Society expedition to Siam to observe the solar eclipse in April, 1875. An interesting account of the expedition occupies 40 or 50 pages, and is followed by one of a walking tour with two friends from Simla north over the Himalayas into Kashmir to the Indus at Leh, then west through Srinagar to Peshawar, a journey of over 600 miles which occupied two months. The 70 pages which the account of this journey occupies are full of graphic descriptions of the scenery, the natives, the difficulties from insubordination of the carriers, the rain, the bad roads, the cold and the scarcity of supplies. With 1875 the biographical details end and we have little more than a modern but equally disappointing version of the formula "the rest of the acts of — and all that he did, and his might, are they not written in the chronicles" of 1906?

The 20 pages of "Episodes" which follow contain some of the stories Schuster could tell so well. But there are many more. What of the glass prism which in the early days of spectrum analysis shewed an unusually generous separation of the sodium lines and was found afterwards to be quite impartial in its duplication of all lines? Or of the visitor to the laboratory in Manchester who claimed to be able to make rain at any time and at any spot he desired and offered (for a consideration) to give a practical demonstration? Or the potential contributor to the building fund for the new physical laboratories who demurred to giving to an institution in which Greek was taught, and the effect on him of Schuster's offer to guarantee that there should be no Greek further than a few letters of the alphabet used in the laboratory?

The 60 pages of "Biographical Byways" are reprints of Schuster's notes on physicists which have appeared at various times in the pages of *Nature*. Those dealing with persons known to the present writer seem to him to give a faithful and vivid picture of each one. Of Balfour Stewart as a lecturer the description on p. 206 is true. He had certain expressions which he used repeatedly, one of which was "thus you see." After a time his students would applaud each repetition, and when on occasions "gentlemen" was added the applause would be more than doubled. The difficulty of understanding Osborne Reynolds towards the end of his professorship, referred to on p. 232, were attributed by one who knew him well to his tendency "when speaking on any subject to be thinking of his *Sub-mechanics of the Universe* and when speaking of one part of the sub-mechanics to be thinking of another part."

The ten pages devoted to Dr Henry Wilde bring out clearly his intense appreciation of orderliness. In his train journeys in non-smoking carriages he invariably objected to any smoking. Although in verbal discussions no argument could move him at the time, a few days later he might remark "there is much to be said in favour of your point of view."

Two photographs of the author taken shortly before he left Manchester, and five of scenery in the Himalayas taken by Lady Schuster in 1908, add materially to the value of a book full of interesting reminiscences written in graphic and concise language, with humour but one serious fault—the "fragments" are not numerous enough. Some Oliver Twist should again be commissioned to go up to the master and say "please sir I want some more."

C. H. L.

Conduction of Electricity Through Gases, by Sir J. J. THOMSON and Prof. G. P. THOMSON. Pp. vi + 608. (Third edition, vol. 2. Cambridge University Press, 1933.) 30*s*.

This volume completes the third edition of the *Conduction*, vol. 1 having appeared in 1928. The first and second editions have long been out of print, and the completion of the third fills a distinct gap in the literature of the subject—a gap which perhaps appeared widest to those who can remember the magnitude and direction of the impulse given to the development of experimental physics by the first appearance of this book.

The new edition is, naturally, much enlarged, and the author index (compiled by Mrs G. P. Thomson) to the second volume alone contains nearly 600 names. The greater part of this volume is given to recent developments, much of the older parts of the work and later refinements of the earlier measurements having been dealt with in the first volume. This second volume opens with a brief and largely familiar chapter on cathode rays, followed appropriately by a new section on the wave properties of these rays. There are long chapters on the collision of electrons with gas molecules and on ionization by positive rays and X-rays, still longer chapters on the complicated phenomena of the discharge in gases at low pressures and of the spark discharge, with shorter ones on reflected and secondary electrons from solid surfaces, on ionization by chemical and other actions, and on the electric arc.

It will be evident from this list of chapters that the authors have not been bound by a too literal interpretation of the title of the book; there are in fact large sections in which the processes of gaseous conduction are at most of secondary importance. The researches described, however, have developed so directly from the type of work which began in the detailed study of conduction in gases, and so largely in the hands of physicists of the same schools, that their inclusion in these volumes appears entirely natural.

It is a pleasure to find that the original character of the book remains so largely unimpaired, in spite of the expansion and rearrangement necessitated by the incorporation of so much new material. In its new as in its older forms, the *Conduction* is above all a book for experimental physicists, and one which is indispensable to research workers in many fields. For readers approaching the subject seriously for the first time it provides an authoritative introduction to many aspects of the most recent developments in atomic physics. New readers will particularly appreciate the wealth of relevant detail with which the more important experimental work is described. Further, as some space is found for accounts of the more significant work of the earlier investigators, the book contains in itself a fairly complete history of a great branch of electrical science. And the history of the thirty years following the first appearance of the *Conduction*—or the forty years since that of the *Recent Researches in Electricity and Magnetism*—is one which should be familiar, at least in outline, to all students of physics.

H. R. R.

Les Phénomènes Élémentaires de la Décharge Électrique dans les Gaz (*Gaz rares*), by Dr Marcel Laporte. Pp. 232. (Paris: Les Presses Universitaires de France.) 75 fr.

This is one of the well-known series of "conférences-rapports de documentation sur la physique" of which a number have already appeared. It deals with the fundamental phenomena underlying the electric discharge with special reference to the inert gases, except that the methods of measuring critical and ionization potentials are for the most part omitted. These have been dealt with in an earlier book of the series by M. Bloch. Within the limitations of the subject chosen the author has given a very clear and satisfactory account of the present state of knowledge. He deals especially fully with the work of Townsend and his pupils, and devotes a good deal of space to considerations of elastic collisions between electrons and gas molecules. He does not, however, refer to the recent work of Arnot and others on the angular distribution of slow scattered electrons, which has thrown so much light on the earlier results of Ramsauer. Space is found for a discussion of the spectra of the inert gases, and tables are given of the terms and principal lines. In view of the importance, on many theories of the discharge, of the electrons ejected from solids by the impact of positive ions more attention might perhaps have been given to an account of experiments on these lines, particularly those of Oliphant.

A feature of special interest is the careful account of the influence of the metastable states of the inert gases on their optical and electrical properties, especially through the action of "collisions of the second kind."

G. P. T.

The Principles of Optics, by Prof. ARTHUR C. HARDY, M.A. and FRED H. PERRIN, S.M. Pp. xiii + 632. (London: McGraw-Hill Publishing Co., Ltd.) 36*s*.

It is claimed by the authors of this very practical and useful book that "it should provide a solid foundation for those who intend to select optics as a career, and at the same time it should furnish an adequate knowledge of the subject in a comprehensible form for those who intend to specialize in other branches of physics or engineering." Its scope is very wide. Starting with the general concepts of geometrical optics and the Gaussian theory, together with chapters on lens aberrations and the diffraction theory of resolving power, the book goes on to deal with the physical optics of radiation and practical sources of light. We then find chapters on the eye, photography, and visual and physical photometry, including colour. Four chapters are devoted to optical materials and the manufacturing processes involved in the production of instruments, and the final series of chapters is devoted to the principal optical instruments. The practical applications of interferometry and polarization are also discussed.

It has been judged advisable to give this summary of contents here because treatises on optics may apparently contain anything from a most detailed and intricate discussion of the design of optical instruments to a superficial galop over their general principles. This book, while perhaps casting its net too wide for great thoroughness, is very practical in its treatment throughout, and contains many useful tables such as those of reflecting power, the sensitometric characteristics of photographic materials, and the like, which will certainly be handy to those using the book as a work of reference.

A first impression regarding the book is that the authors are most successful in the physical-optics and photometric sections. Prof. Hardy's well-known work on the applications of photo-electric cells will lead most readers to expect an excellent treatment of physical photometry, and they will not be disappointed. Opinions may differ, however, in regard to the scope of the geometrical-optics sections, and it may be doubted whether the "solid foundation" for those entering "optics as a career" has in reality been laid. If the word "optics" implies the studies of an ophthalmic optician the scope is ample, but the treatment is not nearly systematic enough for any serious student of optical instruments. It will not be sufficient for him to accept the optical sine theorem without proof, or to learn that "a mathematical expression for the resolving power of a prism can be readily derived." A great deal of modern physical theory is intellectually unsatisfying, like the pieces of a badly fitting puzzle. This is inevitable and we accept it as a necessary stage in the evolution of various subjects, but where intellectual satisfaction which might be given to the student is denied him we encourage loose habits of thinking, and tacitly consent to the view that the satisfaction of the mind is of less importance than the production of microscopes and binoculars. It must be admitted, however, that it is easier to offer this criticism than to write an optical text-book against which it could not be made.

The authors write accurately throughout from a thorough knowledge, and errors are hard to find. (One which might be noted is the incorrect labelling of the image surfaces in figure 47). There must be very few who could not read the book without widening their knowledge of the subject, and it can be thoroughly commended as a general work of reference.

In view of the contemporary discussion of optical signs and conventions, it may be of interest to note that the following statement of the sign convention is given (we quote in part only): (1) Draw all figures with the light incident on the reflecting or refracting surface from the left. (2) Consider the object distance s or PV positive when P is at the left of the vertex. (3) Consider the image distance s' or VP' positive when P is at the right of the vertex. The fundamental equation for refraction at a curved surface therefore appears in the form:

$$\frac{n'}{s'}+\frac{n}{s}=\frac{n'-n}{R}.$$

The two focal lengths of a system are given the same sign, but the dioptric power is not used in the systematic treatment of lens theory, which avoids the more complex questions such as those of combined reflecting and refracting systems.

L. C. M.

The Form and Properties of Crystals: an Introduction to the Study of Minerals and the use of the Petrological Microscope, by A. B. DALE, M.A. Pp. x + 186. (London: Cambridge University Press.) 6*s*.

This account of crystals, their properties, and the methods by which these are investigated, is worthy of commendation. It is evident that every effort has been made to state the subject-matter in the simplest possible way, the similes in particular being extremely well chosen. Examples of these are the Great Pyramid, a match-box and a book to illustrate questions of symmetry; and the appearance of a new-mown lawn is particularly suitable for giving an idea of repeated twinning.

One of the most useful sections is that dealing with stereographic projections. It is certainly the best account of a subject which gives much difficulty to students and which is either ignored or treated inadequately by most writers. Excellent also is the attempt to explain physical properties such as cleavage; even if the suggested explanation is not altogether convincing, it is something to have the problem recognized.

The illustrations are good and give evidence of much thought and careful preparation; it is therefore unfortunate that some of the crystal drawings are slightly out of position, as, for example, in the case of figure 28.

To some minor points exception may be taken. Talc does not seem to be quite at home with the amphiboles. If in Mohs' scale "each mineral is harder than the one immediately below it," it is surely desirable to place diamond at the top of the table and talc at the bottom. Rotating and revolving are not quite the same thing. There is some uncertainty regarding ordinates and abscissae.

However, even the sun has spots, and these small defects should not obscure the fact that the book will be definitely useful in the hands of an earnest student who uses it to *supplement* his studies of actual crystals, models, and thin sections.

H. G. S.

Hydrodynamics, by Sir HORACE LAMB, M.A., LL.D., Sc.D., F.R.S. Pp. xv + 738. (Sixth edition. London: Cambridge University Press.) 45*s*.

What was effectively the first edition of this work was published in 1879 and the fifth edition in 1924. Every student of the subject must feel a personal debt of gratitude to the author for the great work which he has done in giving the world this magnificent exposition of the mathematical theory of the motion of fluids, and every student will rejoice at the abundant evidence supplied by this last edition that the author's powers of exposition still flourish with undiminished clarity, judgment and vigour. The book is beautifully printed and bound, and the present edition reproduces all the clear and useful diagrams of the fifth edition, with the exception of Froude's sketch of the surface waves due to the bows of a ship (§ 256). The reviewers of previous editions of this work have said everything that can be said in its praise, and all that can be usefully attempted by the present writer is a sketch of the new matter introduced in the present edition.

Probably the most important of the new sections are those which bear on problems of aeronautics. The now famous theorem of Kutta and Joukowski giving the "lift" on an aerofoil in terms of the circulation is proved in § 72b by an elegant method due to Blasius and in § 370b by another method. The approximate treatment of the "boundary layer" due to Prandtl, Blasius and Kármán is given in §§ 371a, b. § 371c gives a brief reference to the effect of turbulence and §§ 371d, e, f, and g study the effect of compressibility. Some related researches by Glauert and G. I. Taylor on the forces on immersed solids are summarized in §§ 134a and 143.

References to some recent work on the theory of tides are inserted in chapters 8 and 9. It is shown that Rayleigh's principle can be used in the approximate calculation of free modes of oscillation (§ 205b). A summary is given of the work of Goldsbrough and Colborne on the dynamical theory of tides (§ 223a), and of the work of Havelock, Green and Lamb on surface waves due to travelling disturbances (§ 256a). § 311a gives a further development of the theory of long waves in an atmosphere in isothermal or convective equilibrium, and § 360 reproduces Rayleigh's investigation of the influence of viscosity in sound waves of permanent type. There are a number of other minor additions, e.g. an appendix to chapter 5 gives the hydrodynamical equations in general orthogonal co-ordinates: §§ 72a and 121a show that the effect at a distance from a moving solid immersed in a fluid is approximately equivalent to a double source; § 166a gives Bjerknes' circulation theorem under meteorological conditions when pressure and density are independent. But the chief additions are those relating to aeronautics and tides, which are summarized above.

This book is a worthy monument to the erudition and powers of exposition of the author. It gives an unrivalled exposition of hydrodynamics regarded as a branch of pure mathematics.

G. T.

The Method of Dimensions, by ALFRED W. PORTER, D.Sc., F.R.S. Pp. vii + 80, with 9 diagrams. (London: Methuen & Co., Ltd.) 2*s*. 6*d*.

This little book describes some of the most familiar applications of the "method of dimensions" or, as Rayleigh preferred to say, the use of the principle of similitude. After "Prolegomena" in chapter 1, the next five chapters relate to the flow of fluids, surface tension, vibrating systems, temperature and heat effects, and electricity and magnetism. The last of these chapters is very brief and omits the interesting recent use of the principle to generalize the Child-Langmuir equation. No reference is made in the text, nor in the bibliography, to the books on the same subject by Bridgeman, Wallot and N. R. Campbell.

The Observatories Year Book, 1930. M.O. 340. Pp. 443. (H.M.S.O., 1933.) £3. 3*s*. 0*d*.

It is always satisfactory to a worker dependent on measurements made at one of the British observatories to know not only that he will find the results given in the year books in a convenient form, but also that there is a carefully written statement of the methods of measurement and of reduction. In how many foreign or dominion publications of upper-air results do we find any definite statement of the method of calibration of the hair hygrometer, or of the amount of lag in the readings of pressure and temperature? Another satisfactory feature is the evidence that this work is carried out by men active in research and is not governed by slavish adherence to routine. Thus instead of finding that the height at which an upper-air temperature or pressure reading was recorded is given as 17 dynamic kilometres—a statement that requires considerable explanation to a physicist unfamiliar with the modern jargon—we are correctly told that the height above mean sea level was such that the geopotential there was 17 kiloleos, a kiloleo being 10^8 c.g.s. units of geopotential. Further evidence of the lively interest of the staff in their work is the amount of their contributions to knowledge: those published during the last five years have included papers on subjects as varied as ground temperatures, magnetic disturbances and sunspot changes, atmospheric rainfall distribution in homogeneous air currents and at surfaces of discontinuity, smoke particles and condensation nuclei, air waves from gunfire, and earthquakes. Among much interesting detail is an example of the way in which the purely scientific becomes the commercially important—the hourly values of magnetic declination of Eskdalemuir are published weekly, primarily for the use of mine surveyors, in *The Colliery Guardian* and *The Iron and Coal Trades Review*. The meteorological department is to be congratulated on this useful volume.

G. T. W.

Données Numériques de Spectroscopie: Spectres d'Émission, par L. BRUNINGHAUS; *Spectres d'Absorption*, par V. HENRI; *Électro-magnéto-optique*, par F. WOLFERS; *Diffusion de la Lumière*, par P. AUGER. Pp. xxi + 1397. (Extracted from vols. 8 (1927–8) and 9 (1929) of *Tables Annuelles de Constantes et Données Numériques*. Paris: Gauthier-Villars et C^ie^, 1932.) £3. 13*s*. 0*d*.

To the many English users of the *Annual Tables* the general features of the present volume will be well known, for it is a rebinding of the spectroscopic sections of two of the later volumes of the full work. This reissue is an excellent idea for which all spectroscopists and many other workers in chemistry and physics cannot but feel grateful to the International Committee and its enterprising general secretary, M. Ch. Marie. It renders a huge mass of collected spectroscopic data available to laboratories (and perhaps even to some individual workers) whose limitations of interests and financial resources preclude them from subscribing to the whole series of volumes of the *Annual Tables* just for the sake of the spectroscopic sections. The volume weighs nearly 8 pounds and contains some 1400 large pages (10½ × 8½ inches) of fairly closely printed matter in the form of notes and tables taken bodily from the original papers. The subjects to which the data relate include line spectra of neutral and ionized atoms, band spectra and Raman spectra of diatomic and polyatomic molecules, and the Zeeman and Stark effects. As is well known, the *Annual Tables* make no pretence to be critical, the fullest possible attention being paid to each paper no matter whether it is, on the one hand, one in which the data are good, the analysis is accurate and the notation universally recognized, or, on the other hand, one in which the data are only moderately accurate, the analysis (if any) is erroneous or incomplete, or the notation known to few besides the author himself. Indeed, in regard to the band spectra of diatomic molecules the volume has the bad luck to deal with papers which appeared before the chaotic state of the notation was resolved by the international adoption of Mulliken's notation of 1929 and 1930; this is inevitable since the printing of the 1927–29 volumes is used for this 1932 volume apparently without resetting. However, the uncritical and heterogeneous nature of the tables need not disturb anyone by whom they are used, as indeed they must be used, in conjunction with later accounts of the subjects concerned. Spectroscopists using, say, the volumes on line spectra and atomic energy states in the McGraw-Hill Company's International Series, or the reports on band spectra published by the American Physical Society and by our own Physical Society, will find the present volume of great value.

W. J.

ROPERTY

THE PROCEEDINGS OF THE PHYSICAL SOCIETY

VOL. 45, PART 4 *July* 1, 1933 NO. 249

539.266:546.22

THE DIFFRACTION OF X-RAYS BY LIQUID SULPHUR

BY A. H. BLATCHFORD, M.SC., Research Student,
Reading University

Communicated by Prof. J. A. Crowther, November 5, 1932. *Read April* 7, 1933

ABSTRACT. The X-ray diffraction effects given by liquid sulphur at various temperatures between 130° and 260° C. are measured. The results indicate that the diffraction is caused by an unstable grouping of atoms of sulphur; the grouping becomes less pronounced with increased temperature, and changes in form gradually up to 220° C., when there is a sudden alteration corresponding to the change from the form S_λ to S_μ. Raman and Ramanathan's theory of X-ray scattering by liquids is found to be applicable to some extent at temperatures near the melting-point.

§ 1. INTRODUCTION

THE investigation described in this paper was undertaken to determine, as far as possible, the structure of sulphur in the liquid state from a temperature of 130° C. to 260° C., this range including the transition stage from the light yellow mobile liquid formed just above the melting-point to the dark brown viscous liquid formed near 200° C. The X-ray diffraction effects were obtained photographically and measured photometrically.

§ 2. EXPERIMENTAL DETAILS

The source of radiation was a Shearer tube, fitted with a molybdenum anticathode. The tube was operated by a 2-kilowatt transformer and took a current of 5-6 mA. at 75,000 V. The rays emerged through an aluminium window 0·05 mm. in thickness, and the beam was cut down by a lead stop 0·2 cm. in diameter before passing into the camera. The camera consisted essentially of a collimator, a cell containing the sulphur, and a film holder. The collimator was made of brass tubing 5 cm. long, fitted at each end with lead discs, bored centrally with holes of diameter 0·15 cm. The cell was made of aluminium foil, 0·01 mm. in thickness, and distance pieces were arranged in it so that the collimated beam of X-rays transversed a thickness of 0·3 mm. of sulphur. The cell and sulphur could be heated electrically to any required temperature, which was measured by a platinum-platinum-iridium thermocouple. The beam of X-rays traversing the sulphur was diffracted, the diffraction haloes being then recorded on a Kodak Duplitized X-ray film.

The production of each photograph was made under as nearly constant conditions as possible, by giving an exposure of 3½ hours at 5 mA. and developing and fixing with solutions of the same strength for equal times. To prevent fogging of the film the central beam was absorbed with a lead disc placed near the film for the main part of the exposure, the lead disc being removed for a few minutes at the end of the exposure in order to record the position of the centre of the halo.

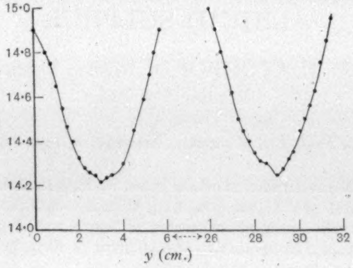


Figure 1.

The photometer for measuring the diameters of the diffraction haloes consisted of a 25 candle-power lamp fitted with a thin cylindrically coiled filament, the light from which was focused on the film under measurement. The light was passed through a water cell to prevent undue heating of the photographic film, and suitable stops prevented any light, excepting a good image of the filament, from falling on the film. A measure of the intensity of light emerging from the film was given by the current produced in a vacuum photoelectric cell. The film was held between two brass plates, which could be traversed by a screw in a plane perpendicular to the incident light, and the position of the film in the holder was adjusted so that observations could be taken for various positions of the filament-image on a diameter of the halo. The deflection x of the galvanometer in the photoelectric cell circuit was plotted against the distance of traverse y of the film, the positions of the diffraction peaks being then shown as minima. Figure 1 shows the type of curve obtained for sulphur just above the melting-point.

The diffraction effects caused by the aluminium cell were first recorded and then photographs were taken for sulphur at temperatures of 130°, 155°, 182°, 221°, 225° and 260° C. By suitable adjustment of the current in the heating coil these temperatures were maintained within 2° C. Each halo was measured along three or four diameters and the probable error of the diameter was computed. The liquid sulphur in the cell was replaced by finely crushed solid sulphur and the diffraction effects were

REPORT ON BAND-SPECTRA OF DIATOMIC MOLECULES,

by W. JEVONS, D.Sc.

ERRATA

(This list includes and replaces those on p. viii and the original errata slip.)

Page 13, line 12 from foot: “He_2 and H_2” should be “He_2, H_2 and N_2”
Page 18, line 8 from foot: “Schrödinger” is misspelt
Page 23, equation (12): the denominator of the term in r_e^2 should be $2r^2$ not $2r$
Page 25, line following equation (23): “3” should be “2”
Page 26, line 2: “energy” is misprinted
Page 27: the second equation in (27) should be $b_3 = -b_2\left(\frac{\alpha\omega_e}{6B_e^2} + 1\right)$
Page 27: after equations (30) the following sentence should be inserted: “The first and second of these, which are based upon equation (12), are not verified by observation, but the third, which is independent of any assumed *U* function, is much more nearly true”
Page 30, line 9 of text: “notation” should be “rotation”
Page 32, line 8 from foot: ν' should be v'
Page 42, line 9: “of” should be inserted after “test”
Page 42, table: “270·25” should be “270·53”
Page 45, line 1: “sets” is misprinted
Page 48, line 1: “$4D$” should be “$4D'$”
Page 51, first line of equations (55): “$[\nu_0 +$ ” should be “$\nu_0 + [$”
Page 62, line 2: “(62)” should be “(58)”
Page 65, line 14 from foot: “molecule” should be “molecules”
Page 67, line 13: “is” should be “are”
Page 69, top of fig. 16 (*d*): “$\omega_e' \gg \omega_e''$” should be “$\omega_e' \ll \omega_e''$”
Page 70, line 10: the second “$r'_{\text{min.}}$” should be “$r''_{\text{min.}}$”
Page 77, line 3: “is indicated” should be inserted after “system”
Page 79, line 16: “$10^8{}_e$” should be “$10^8 e$”
Page 82, line 6 from foot: “X^+” should be “X'”
Page 82, line 4 from foot: “excitation” should be “ionization”
Plate II, strip 5: “? CO^+” should be “? CO_2^+”
Page 84, line 13: “A and a” should be “μ and α”
Page 95, middle: after the words “hence the relative intensities are” the first “$^2D_{2\frac{1}{2}}$” should be “$^2D_{1\frac{1}{2}}$”
Page 96, line 29: “$\ldots J+1$” should be “$\ldots J$”
Page 98, bottom-left of fig. 24: “$\frac{2}{3}A$” should be “$\frac{3}{2}A$”
Page 104, line 4: “7, 9” should be “2, 10”
Page 104, line 25: “$S_{\frac{1}{2}}$” should be “$^2S_{\frac{1}{2}}$”
Page 112, fourth line of note (1): “$\sigma^5\pi^4$” should be “$\sigma^9\pi^4$”
Page 113, line 4: “$3p\pi$” should be “$3d\pi$”
Page 114, line 14: “unexpected” should be “unexcited”
Page 119, line 9 from foot: “limited” should be “limiting”
Page 120, line 12: “even or odd” should be “odd or even”
Page 127, line 1: “field” should be inserted after “magnetic”
Page 129, first column in table: the figures $+2$, $+1$, -1 and -2 following “$J' - J''$” should be -2, -1, $+1$, $+2$ respectively
Page 130, fig. 32 (ii): the first “$^1\Sigma^-_u$” should be “$^1\Sigma^+_u$”
Page 143, note (ii): “$^3P_1$” should be “$^3P_0$”
Page 153, line 21: “molecule” should be inserted after “homonuclear”
Page 157, fig. 39(*a*): “R_1” and “R_2” should be interchanged
Page 158, equations (89): the sign before “$\frac{1}{2}\gamma(K+1)$” should be $-$, not $+$
Page 167, third and fourth columns of table: the entries for NO γ should be “$^OP_{12}, P_1; P_2, Q_2$” and “$\nu_{Q_2\,\text{head}} - \nu_{P_1\,\text{head}}$”
Page 194, line 11: “$-\frac{1}{4}x_e\omega_e$” should be deleted
Page 194, equations (114): the lower line should be

$$“= \omega_e^2/4x_e\omega_e - \tfrac{1}{2}\omega_e + \tfrac{1}{4}x_e\omega_e = \tfrac{1}{2}(\omega_e - x_e\omega_e)\,v_{\text{max.}}\ \text{cm}^{-1}”$$

Page 195: line 2 should be “$\frac{1}{2}(2167{\cdot}4 - 12{\cdot}7)\ 84{\cdot}8\ \text{cm}^{-1} \equiv 11{\cdot}3$ volts”

[OVER

Page 195, line 23: "0·81 volt...less exact than" should be "0·96 volt (not 0·81 as stated in the original paper **13 a**) in close agreement with"

Page 195, line 38: "0·81" should be "0·96"

Page 216, equations (129 *b*) and (130): "ν" should be "ν_r"

Page 223, line 12 from foot: "C^{12}" should be "C^{13}"

Page 225, second line below table: "$N^{15}O^{16}$" and "$N^{14}O^{18}$" should be interchanged. This error occurs in the original paper **128 s**

Page 229, line 6 from foot: "fluorescence" is misprinted

Page 257, fig. 65 (iii): "$\frac{1}{2}\Delta\nu$" should be "$\frac{1}{2}\Delta\nu_n$"

Page 275, note * on CH: "and apparently belong to" should be "(0,0), and are the 1,1 and 1,0 bands, respectively, of"

Page 282: for the ground state of Na_2, "0·726 +" and "0·15433" should be "0·726 −" and "0·15431"

Page 284: for SiN the entries under (ii) should be "1031·01 16·743 +" for state B (not A), and "H 1032·3 6·4" for state A

Page 286: for the ground state of BO, "10·71" should have been "11·71" but better data have since become available

Pages 288–9, under (i) and (vii): for SnO, "25911" should be "29511"

Page 290: for each state of SO, "$^2\Sigma$" should be "$^3\Sigma$"

Page 290: for the ground state of S_2, "2·75" should be "2·91"

Page 300: line 7 from foot: reference letter "**w**" should be "**u**"

June, 1933

photographed for comparison. Finally, the cell was filled with finely crushed sodium chloride to determine, from the diffraction, the distance p from the cell to the photo- p
graphic plate in the camera.

Well-marked diffraction haloes were obtained just above the melting-point, the haloes becoming more diffuse and fainter as the temperature increased. This increased the difficulty of estimating the positions of the diffraction peaks with increase of temperature, producing a decrease in the accuracy of measurement of the diameters of the haloes. From Bragg's law of diffraction, the diffraction haloes may be taken to indicate an effective periodicity d of electron-density-distribution in d
planes, and in all directions in the liquid, given by

$$\lambda = 2d \sin \theta,$$

where θ is the glancing angle for the given distribution of electrons, $\tan 2\theta$ being θ
then given by r/p, where r is the radius of the halo and p, measured as above, is r
6·40 cm.

Both the diffraction rings given by crushed salt and solid sulphur showed that only the $K\alpha$ radiation of molybdenum was recorded on the photographs. Hence d was calculated from the equation:

$$0{\cdot}712 = 2d \sin \left(\frac{1}{2} \operatorname{arc} \tan \frac{r}{p} \right).$$

§ 3. THEORIES

There are two main theories of X-ray diffraction in liquids to which the results obtained in the present investigation may be applied. The theory of Stewart postulates that in certain organic liquids the molecular forces and shapes are such that an entirely random distribution is not produced, and, in fact, that unstable groupings are produced throughout the liquid, and that in such groups there are recurring planes of maximum density of distribution of electrons. The quantity d, found above, then refers to the distance of separation of such planes.

On the other hand, the theory of Raman and Ramanathan shows that, if the molecules are assumed to be symmetrical, there will be a maximum diffraction of X-rays at an angle given by Bragg's equation $\lambda = 2d \sin \theta$, where d is the average distance of separation of the molecules. The results will, therefore, be applied to see if d can be more favourably interpreted as an inter-planar distance, or an average distance of separation of scattering centres.

A third way in which diffraction in liquids has been treated is based on the Ehrenfest formula for the scattering of X-rays by electrons in pairs, at a distance s s
apart. On this theory the mean distance between scattering centres, assumed to be atoms or molecules, is given by

$$s = 7{\cdot}72/(4\pi\lambda^{-1} \sin \theta) = 1{\cdot}23d.$$

The mean distance d_0 of separation of the atoms of sulphur may be calculated, the d_0
closest packing in spheres being assumed. It can be shown to be equal to $1{\cdot}33\,(M/\rho)^{\frac{1}{3}}$ Å.,
where M is the atomic weight of sulphur on the hydrogen scale and ρ is its density. M, ρ

Sulphur in the liquid state has a molecule containing 8 atoms, hence the
d_1 average distance d_1 of separation of molecules is $2d_0$.

§ 4. RESULTS AND DISCUSSION

The results obtained are shown in table 1 and the values of d and d_0 are plotted in figure 2.

Table 1

T (° C.)	r (cm.)	d (Å.)	d_0 (Å.)	S (Å.)
130	1·257 ± ·003	3·68 ± ·01	3·47	4·52 ± ·01
155	1·234 ± ·004	3·74 ± ·01	3·48	4·58 ± ·01
182	1·235 ± ·006	3·74 ± ·02	3·49	4·62 ± ·02
221	1·202 ± ·010	3·84 ± ·04	3·49	4·72 ± ·05
225	1·165 ± ·006	3·96 ± ·02	3·51	4·87 ± ·02
260	1·137 ± ·014	4·06 ± ·05	3·52	4·99 ± ·06

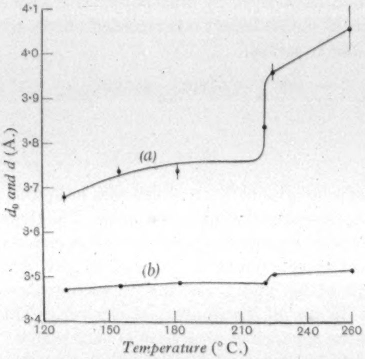


Figure 2. Values (*a*) of d and (*b*) of d_0.

It is seen that there is a gradual increase of the distance d with temperature up to 220° C., the rate of increase becoming less rapid as 220° C. is approached. At this temperature there is a sudden increase in d, which rises from approximately 3·79 Å. at 220° C. to 3·95 Å. at 223° C. There is thus a change of 4·2 per cent with 3° C. rise of temperature, after which d increases with temperature as before.

The photograph taken with crushed solid sulphur showed two main diffraction rings having radii of 1·40 cm. and 1·15 cm. There is thus a similarity between the solid and liquid diffraction; the halo produced at 130° C., for example, has a radius which is close to the mean of the radii of the main diffraction rings for the solid. The flatness of the minima of the graphs also suggests the possibility of diffraction corresponding to more than one interplanar distance, but the photometer's resolving power was not sufficient to show such diffraction effects clearly, if present.

Sulphur crystallizes in the rhombic bipyramidal system, and work by W. H. Bragg* and Wigner and Mark† has shown that the crystal unit consists of 128 atoms of sulphur, arranged as 16 interpenetrating lattices of the rhombic bipyramidal element, having a equal to 10·61, b to 12·87, and c to 24·56 and containing 8 atoms of sulphur arranged as shown in figure 3. The rings obtained for solid sulphur correspond to diffraction by the (040) and (222) planes, the glancing angles obtained experimentally being $6^\circ 10'$ and $5^\circ 6'$. The mean value $5^\circ 33'$ of θ obtained for sulphur at 130° C., and the distinct possibility that it may be an average value for two maximum diffraction angles (see figure 1), strongly suggest that the forces determining the crystal structure of sulphur are still effective to a marked degree in the liquid structure just above the melting-point, and that grouping of the atoms to form an unstable lattice occurs. Further, the liquid diffraction at 130° C., although it is more diffuse than that of the solid sulphur, is intense, showing that the grouping of atoms is a general and well-marked feature of the structure at temperatures just above the melting-point. The effect of temperature will now be considered.

If the measurement d is an interplanar distance, or an average distance of separation of molecules, it is to be expected that it will show some relation to the expansion of sulphur. The volume of 1 gm. of sulphur at various temperatures in the range under consideration is plotted in figure 4 from data from the *International Critical Tables*. There is seen to be a discontinuity in curve (a) of figure 2, and a corresponding discontinuity must also be assumed from the points plotted in figure 4.

Numerical comparisons may be made as follows:

From 134° *C. to* 210° *C.*

Figure 2 (a). Concave downwards with an increase in d of 2·3 per cent.
Figure 4. Concave downwards with an increase in $1/\rho$ of 1·9 per cent.

Near 220° *C.*

Figure 2 (a). A sudden increase in d of 4·1 per cent.
Figure 4. A sudden increase in $1/\rho$ of 0·7 per cent.

From 225° *C. to* 260° *C.*

Figure 2 (a). An increase in d of 2·5 per cent.
Figure 4. An increase in $1/\rho$ of 1·3 per cent.

If the diffraction in the liquid is caused by an unstable modification of the crystal structure, and corresponds to diffraction by the (040) and (222) planes in the crystal, the percentage increase in d denotes the percentage increase in the dimensions of OB and OP where P is the foot of the perpendicular to the (222) plane ABC, figure 3. It may reasonably be assumed that increased kinetic energy of the sulphur atoms tends to produce a more random distribution, gradually obliterating the effect of forces tending to produce regular grouping of the atoms, and therefore that as the temperature is increased, the atoms still group in roughly the same form, but the lattice is modified so that the various interplanar distances become more nearly equal. This might come about, for example, by the atoms in the planes *OAFB* and *DCEG* moving further apart on the average, and the distance of separation *DB* of such planes being reduced. The photographs give evidence of the distance corresponding to *OB* increasing, but the distance *DB* is not shown by the diffraction effect in the liquid.

---

* *Proc. R. S.* A, **89**, 575 (1914).

† *Z. Phys. Chem.* **111**, 398 (1924).

Applying this theory to the results obtained it is seen that there is an increase in *OB* of approximately 2·3 per cent from 134° to 210° C., and from the symmetry of atoms in the plane *OABF* it may be assumed that there is an increase in the direction *OA* of about the same magnitude. This is equivalent to assuming that atoms in (001) planes, e.g. *O* and *A*, will be displaced from an atom *K* in approximately the same proportion with increased temperature. Now there is an increase of $1/\rho$ equal to 1·9 per cent, and therefore an average decrease in *DB* of (4·6 − 1·9) or 2·7 per cent will be required to explain this result. Thus it seems feasible that as the temperature rises the unstable lattice of sulphur gradually expands along *OA* and *OB* and contracts along *OC*. The photographs indicate that at somewhere near 220° C. there is a comparatively sudden change in *d*, which must mean that the increased kinetic energy of the atoms of sulphur makes possible a new unstable lattice. Thus, on the assumptions made before, there will be something in the nature of a fairly sudden increase with temperature in *OA* and *OB* of 4·1 per cent each, and the increase of 0·7 per cent in $1/\rho$ requires a decrease in *OC* of (8·2 − 0·7) or 7·5 per cent. The effect of increase of temperature from 130° C. to 220° C. is repeated above 220° C. in a more marked manner, there being an increase in *OA* and *OB* of 2·5 per cent and a decrease in *OC* of (5·0 − 1·3) or 3·7 per cent.

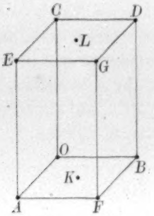


Figure 3.

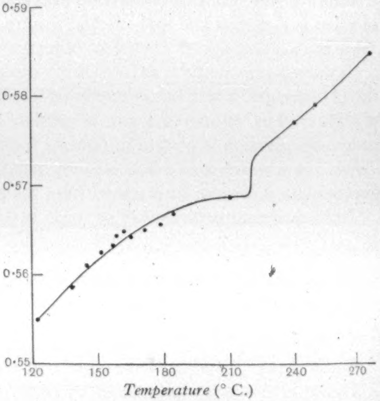


Figure 4.

In figure 5 *d* is plotted against $\rho^{-\frac{1}{3}}$. If the diffraction effects were simply due to a random orientation of atoms or molecules *d* would be directly proportional to $\rho^{-\frac{1}{3}}$.

Experimentally a curve is found with a distinct break indicating the change in structure near 220° C.

The effect of change of temperature on the diffraction of X-rays by organic liquids has been investigated by Skinner, who found increases with temperature in the planar distances occurring in unstable groups of molecules, which were, in some cases, three times the coefficient of expansion, and actual decreases of interplanar distances with increase of temperature were also measured. The above discussion points to similar effects occurring in an unstable lattice of atoms of sulphur in the liquid state.

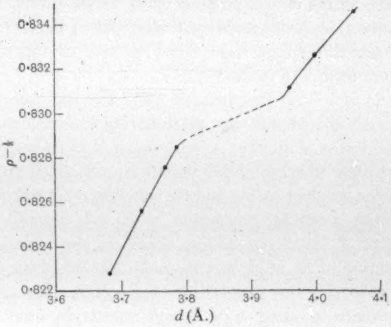


Figure 5.

Applying the results to the theory of Raman and Ramanathan we see from table 1 that the mean distance d_1 of separation of molecules of sulphur at 130° C. $= 2d_0 = 6{\cdot}94$ Å., a value which is hopelessly out of agreement with the value 3·68 Å. found by experiment at this temperature. The diffraction, therefore, does not appear to be due to random molecular distribution. If, however, the average distances of separation of the sulphur atoms are examined, more definite conclusions can be reached; d_0 and T are plotted at (*b*) in figure 2, and it is seen that the value of d_0 is about 6 per cent lower than that of d at 130° C., and that as the temperature increases the values of d and d_0 diverge slightly from one another, d being about 12 per cent greater than d_0 at 260° C. If the theory of Raman and Ramanathan were accurately true d would be equal to d_0 at all temperatures, and from the present experiments it may therefore be concluded that the theory is more nearly true for the case of sulphur near the melting-point. It is seen, however, that the large jump in the value of d near 220° C. cannot be accounted for on Raman and Ramanathan's theory, and the rough agreement found therefore seems to be arbitrary. Also, from the magnitude of d by experiment, and d_0 by calculation, it is again evident that the diffraction is related to interatomic distances, and not to intermolecular distances as in the case of organic liquids*.

---

* *Phys. Rev.* **30**, 232 (1927); **31**, 20 (1928); **32**, 153 (1928).

Considering now the theory based on the Ehrenfest formula, if the scattering centres are taken as being molecules S should have the value 6·94 Å. at 130° C. as previously calculated, whereas it is found by experiment to be 4·52 Å. Here, as with Raman and Ramanathan's theory, the facts fit the theory better if the scattering centres are taken to be single atoms. Even then the value 4·52 Å. of S is about 25 per cent higher than the value 3·47 Å. of d_0. Also from table 1 it is seen that the value of S increases more rapidly with temperature than that of d_0. The experiments, therefore, indicate that the Ehrenfest formula is inapplicable to the liquid state, and that the theory of Raman and Ramanathan is more applicable near the melting-point, the scattering centres in the case of sulphur being single atoms. The theory of unstable grouping gives most satisfactorily the structure of liquid sulphur just above the melting-point and the type of changes which may be expected to occur for a range of temperature from 130° to 260° C.

The results fit in well with the chemical facts and the theory which has been deduced. The generally accepted theory, proposed by A. Smith and W. B. Holmes*, is that there are two forms of sulphur, the one soluble in carbon bisulphide, designated S_λ, and the other insoluble, designated S_μ. A small proportion of S_μ is formed as soon as the sulphur melts, and the amount increases as the temperature rises according to the reversible reaction $S_\lambda \rightleftharpoons S_\mu$. At 160° C. the sulphur is a saturated solution of S_μ in S_λ containing about 12 per cent of S_μ, and above 160° C. supersaturation of S_μ in S_λ occurs, and a second phase appears consisting of a solution of S_λ in S_μ, the proportion of S_λ decreasing as the temperature increases. The presence or absence of foreign matter in small quantities affects to a considerable extent the temperature of greatest viscosity. Further, it has been shown by Trillat† that if the structure of viscous sulphur is stabilized by quenching in water, exposure to X-rays greatly accelerates the change to the ordinary soluble form. Hence the action of X-rays in the reversible reaction $S_\lambda \rightleftharpoons S_\mu$ is to favour the formation of S_λ, thus producing the transition point at a higher temperature in the present experiments. The fact that transition from S_λ to S_μ occurs at 220° C. instead of near 160° C. is therefore readily explained. This leads to the conclusion that S_λ is the form of sulphur in which the atomic forces produce unstable grouping, as described above, and that S_μ is a form of sulphur in which the unstable grouping is changed in the manner previously suggested. The increased viscosity of S_μ form may, in this case, be caused by the increased interpenetration of the rhombic bipyramidal elements containing 8 atoms, which would be expected to produce a more cohesive liquid.

§ 5. ACKNOWLEDGMENT

In conclusion the author wishes to thank Prof. J. A. Crowther for suggesting the problem discussed in this paper, and for the helpful interest he has shown during the course of the work.

---

* J. W. Mellor, *Theoretical Chemistry*, **10**, 46 (1927).

† *Comptes Rendus*, **192**, 559–61 (1931).

535·338

THE HYPERFINE STRUCTURE OF PERTURBED SERIES

BY E. GWYNNE JONES, Beit Scientific Research Fellow,
Imperial College, London

Communicated by Prof. A. Fowler, F.R.S., February 2, 1933. Read April 7, 1933

ABSTRACT. A discussion of the hyperfine structures of the terms in perturbed series is given, and rules governing such effects are derived. It is found that these rules are not analogous to those obtained from the analysis of multiplet structures.

---

§ 1. INTRODUCTION

FROM a discussion* of term series which do not obey the usual Ritz formula it has been shown that when an atom has states of nearly equivalent energy arising from different electron configurations these states may suffer mutual perturbation. Experimentally the perturbations are recognized as apparent "repulsions" between terms having the same L and J values. From their analysis Shenstone and Russell were able to represent a series, perturbed by a foreign term ν_0 of the same type, by the formula

$$\nu_n = R/(n+\delta)^2; \qquad \delta = (\mu + \alpha\nu_n + \beta/\nu_n - \nu_0) \qquad \ldots\ldots(1),$$

where R, n, μ and α are the usual constants of the Ritz formula and the expression $\beta/(\nu_n - \nu_0)$ is due to the perturbing effect. It appears that the constant β, which governs the magnitude of the perturbation, is essentially the same for all the members of mutually perturbing multiplets (cf. the $^3D_{1,\,2\text{ and }3}$ of Ca I, for which $\beta_1 = -85$; $\beta_2 = -86$ and $\beta_3 = -90$). On the other hand, β appears to be slightly different for the various isotopes of a given element. Later it was found† that when terms of different types lie so near together that their mutual separation is comparable with their hyperfine separations, perturbations may occur between hyperfine levels having the same quantum numbers. In the following discussion it will be shown that an extension of the above viewpoints affords an explanation of several anomalies in the results of hyperfine-structure investigations.

ν_0

R, n, μ, α
β, ν_n

§ 2. THE HYPERFINE STRUCTURE OF THE $6s.mp.{}^1P_1$ SERIES OF Hg I

The analysis‡ of the hyperfine structures occurring in the mercury spectrum shows that the terms of the two odd isotopes, 199 and 201, possess hyperfine structures arising from the interaction of nuclear magnetic moments, I_{199} equal to $\frac{1}{2}$ and

---

* A. G. Shenstone and H. N. Russell, *Phys. Rev.* **39**, 415 (1932).

† H. Schüler and E. G. Jones, *Z. f. Phys.* **77**, 801 (1932).

‡ H. Schüler and J. E. Keyston, *Z. f. Phys.* **72**, 423 (1931); H. Schüler and E. G. Jones, *Z. f. Phys.* **74**, 631 (1932).

I_{201} equal to $\frac{3}{2}$, with the total moment J of the external electrons of the atom, and that the terms of the even isotopes—only 198, 200, 202 and 204 come into question for spectroscopy—are single, indicating the absence of nuclear magnetic moments. The hyperfine structure of the term $6\,^1P_1$ is shown diagrammatically in figure 1, from which it is seen that the levels of the odd isotopes are grouped regularly about the unresolved terms of the even isotopes, together with which the optical "centres of gravity" of the levels of the odd isotopes fall. Important features of the mercury hyperfine structures are that (*a*) the levels of Hg^{201} are always inverted with respect to those of Hg^{199}, cf. figure 1; and (*b*) in terms characterized by $J = 1$ the total hyperfine separations for the odd isotopes are, in the absence of disturbing influences, the same*. In some terms, generally those associated with *s*-electrons, a further complication enters, whereby the levels of the several even isotopes (although individually not split, as no nuclear magnetic moments are present) are separated, in the order of their mass-numbers, by the operation of the isotopic displacement effect.

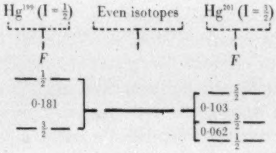


Figure 1. The hyperfine structure of the level $6\,^1P_1$ of Hg I.

In the $6s.mp\,^1P_1$ sequence of Hg I, the lowest member, $6\,^1P_1$, has hyperfine structure separations $\Delta\nu \approx 0{\cdot}175$ cm.$^{-1}$ for the odd isotopes and the levels of the even isotopes are coincident; this measured structure is in agreement with the structures of the other members of the $6s.6p$ multiplet. It would be expected, both on experimental and theoretical grounds, that the higher $^1P_1$ terms should possess structures and isotopic displacements smaller than those of the lowest term. The $8\,^1P_1$, which is, however, perturbed† by the presence of $d^9.s^2.6p.\,^1P_1$ some 1100 cm.$^{-1}$ lower in the energy diagram, shows an anomalous increase in hyperfine separation to $\Delta\nu = 0{\cdot}385$ cm.$^{-1}$ and in isotopic displacement to 0·060 cm.$^{-1}$; the hypothetical unperturbed $8\,^1P_1$ should have equal separations not greater than 0·175 cm.$^{-1}$ for both odd isotopes, see figure 2. Considering first the perturbation in Hg^{199} and remembering that a perturbation is apparent as a repulsion of terms with the same quantum numbers, it is clear that the observed increase in the hyperfine separation can only occur if the mutual perturbation of the ($F = \frac{1}{2}$) levels is greater than that of the ($F = \frac{3}{2}$) levels, i.e. $\Delta_{\frac{1}{2}} > \Delta_{\frac{3}{2}}$, and, as the other quantities in equation (1) are the same for all the hyperfine levels concerned, $\Delta \propto \beta$, whence, setting $\beta = \beta_{(J)} + \beta_{(F)}$ so that $\beta_{(J)}$ shall be the perturbation constant for the centre of gravity of the level and $\beta_{(F)}$ shall measure the second-order differential effect, we find that

$$\beta^{199}_{(F)} > \beta^{199}_{(F+1)} \dots [I = \tfrac{1}{2}; \quad g(I) > 0] \qquad \dots\dots(2).$$

---

* Schüler and Jones, *loc. cit.*

† Shenstone and Russell, *loc. cit.*

Similarly, for Hg^{201}, the mutual perturbation of the $(F=\frac{5}{2})$ levels must be greatest and that of the $(F=\frac{1}{2})$ levels least, thus,

$$\beta^{201}_{(F)} < \beta^{201}_{(F+1)} \ldots [\mathrm{I}=\tfrac{3}{2}; \quad g(\mathrm{I})<0] \qquad \ldots\ldots(3).$$

Also the various levels are so perturbed that the Landé interval rule, necessarily obeyed by the unperturbed term, holds for $8\,^1P_1$ after the perturbation.

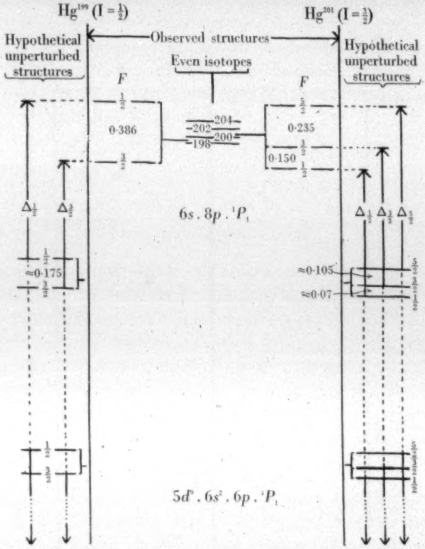

Hg¹⁹⁹ (I = ½)
Hg²⁰¹ (I = 3/2)
Hypothetical unperturbed structures
Observed structures
Even isotopes
Hypothetical unperturbed structures
F
F
½
3/2
0·386
204
202
200
198
5/2
3/2
½
0·235
0·150
Δ½
Δ3/2
Δ½ Δ3/2 Δ5/2
≈0·175
≈0·105
≈0·07
6s . 8p . ¹P₁
5d⁹ . 6s² . 6p . ¹P₁

Figure 2. The perturbation of the hyperfine structure of $8\,^1P_1$ of Hg I.

The appearance of an isotopic displacement in $8\,^1P_1$, see figure 2, indicates that the perturbation constant β is different for the nuclei of different isotopes and, because the term of Hg^{204} lies highest in the diagram when the perturbation is from below,

$$\beta^{204} > \beta^{202} > \beta^{201} > \beta^{200} > \beta^{199} > \beta^{198} \qquad \ldots\ldots(4),$$

where the constants for the odd isotopes refer to the perturbation of the respective optical centres of gravity.

The hyperfine structure of the unperturbed $d^9.s^2.p.\,^1P_1$ cannot be estimated, as this term is influenced by the whole of the $^1P_1$ series in the midst of which it lies.

§3. THE HYPERFINE STRUCTURES OF THE ^2D-TERMS OF Pb II

Two sets of ^2D-terms, arising respectively from the configurations $6s^2.md$ and $6s.6p^2$, have been recognized in the Pb II spectrum. The four lowest members, all of which have been investigated* for hyperfine structure, are unusual in that the $6s^2.6d$ doublet lies entirely within that of the $6s.6p^2$ configuration; see figure 3.

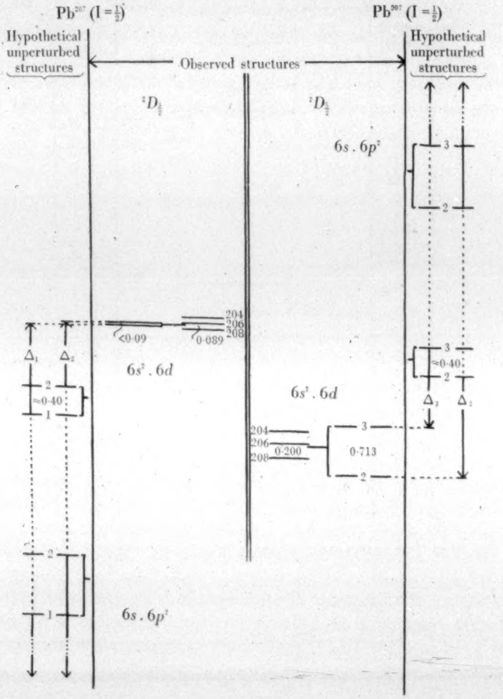

Pb²⁰⁷ (I = ½)
Hypothetical unperturbed structures
Observed structures
Pb²⁰⁷ (I = ½)
Hypothetical unperturbed structures
²D_{3/2}
²D_{5/2}
6s . 6p²
204
206
208
<0·09
0·089
Δ₁
Δ₂
6s² . 6d
2
≈0·40
1
3
≈0·40
2
Δ₁
Δ₂
6s² . 6d
204
206
208
0·200
3
0·713
2
3
2
2
1
6s . 6p²

Figure 3. The perturbation of the hyperfine structures of the $6s^2.6d.^2D$ terms of Pb II.

The separation of terms with similar J-values is such that selective perturbations of their structures might be expected to occur.

The analysis of the hyperfine structures in the lead spectra indicates that the even isotopes 208, 206 and 204 have zero nuclear magnetic moments, and that all the resolvable terms of Pb^{207} are double; whence $\mathrm{I}_{207} = \frac{1}{2}$.

---

* H. Kopfermann, *Z. f. Phys.* **75**, 363 (1932); H. Schüler and E. G. Jones, *Z. f. Phys.* 75, 563 (1932); J. Rose and L. Granath, *Phys. Rev.* **40**, 760 (1932).

The presence of a perturbation is evident from the abnormalities of the $6s^2 . 6d$ terms in respect to both coarse and hyperfine structure—the doublet is inverted and the hyperfine separations and isotopic displacements of ${}^2D_{\frac{5}{2}}$ are much larger than those of ${}^2D_{\frac{3}{2}}$. If any difference were expected between these terms, it would be that the hyperfine separation should be slightly larger for ${}^2D_{\frac{3}{2}}$. The perturbation which causes these anomalies is represented in figure 3. As $6d . {}^2D_{\frac{3}{2}}$ is perturbed from below and $6d . {}^2D_{\frac{5}{2}}$ from above, it is clear that their structures will be influenced in opposite senses; the fact that the structure of the former has been decreased and that of the latter increased leads to the result that the perturbation constant is greater for the hyperfine level of the smallest F value, or

$$\beta^{207}_{(F)} > \beta^{207}_{(F+1)} \ldots [\mathrm{I} = \tfrac{1}{2}; \quad g(\mathrm{I}) > 0] \qquad \ldots\ldots(5).$$

The observed perturbation of the isotopic displacements again requires, as for Hg, that the perturbation constant be greatest for the heaviest isotope:

$$\beta^{208} > \beta^{207} > \beta^{206} > \beta^{204} \ldots \qquad \ldots\ldots(6).$$

If it be assumed that the magnitude of the perturbation of the isotopic displacements is approximately the same for both sets of terms, then the unperturbed displacement effect of the $6d$ electron will be about 0·14 cm.$^{-1}$. In Pb I, terms involving a $6d$ electron have isotopic displacements of approximately 0·030 cm.$^{-1}$, which is equivalent to an effect of about 0·12 cm.$^{-1}$ in the first spark spectrum. This agreement in order of magnitude also supports the view that the two sets of ${}^2D$-terms suffer mutual perturbations.

§4. OTHER SERIES WITH PERTURBED HYPERFINE STRUCTURES

Many series in the spectra of other elements show the characteristic perturbations described above. The lowest terms of the $3s . mf . F$ series in Al II, which are strongly perturbed by terms of the $3p . 3d$ configuration*, all possess a doublet structure, which, in view of the above discussion, may be regarded as a greatly perturbed hyperfine structure†. In the arc spectrum of lead the $p\,{}^3P_1$ series show slight perturbations in their hyperfine structures; owing to the fact that each term is perturbed by the whole $s\,{}^3P_1$ series the net effect is therefore small and no isotopic displacements are produced. The hyperfine structures of Tl II also show the presence of many small perturbations in the higher members.

§5. DISCUSSION

The above examples show conclusively that the rules obtained for the mutual perturbations of hyperfine structure levels are not what would be expected from a consideration of analogous perturbations in the coarse-structure terms. Hyperfine levels, of given J and I, have perturbation constants $\beta_{(F)}$ which show a complicated dependence upon their F values, whilst coarse-structure levels, of given L and S, have the same perturbation constant which is independent of their J values. This result is very surprising, for it has always been possible to derive rules applicable to hyperfine structures by the substitution of J, I and F for the quantum numbers L, S and J, respectively, in the corresponding rules for coarse structures. In particular, the usual intensity and interval rules, in their modified form, are strictly valid in hyperfine structures.

---

* Shenstone and Russell, *loc. cit.*

† This would indicate that Al^{27} has a nuclear moment I equal to $\frac{1}{2}$.

The selective perturbations found in mercury show unambiguously that the nature of the effect is governed by the sign of the g (I) factor—the ratio of the magnetic to mechanical moments—of the nucleus concerned. The perturbations in Hg^{199} and Pb^{207} are particularly interesting as both atoms have the same nuclear moments and similar g (I) factors: the same variation of $\beta_{(F)}$ is obtained in both cases, whether the hyperfine levels are normal (Pb^{207}, figure 3) or inverted (Hg^{199}, figure 2).

The differential perturbation of the terms of the individual isotopes is also independent of their relative energies, for in lead the isotopic displacements are inverted with respect to those in mercury; nevertheless the terms of the heaviest isotopes suffer the greatest perturbation in both elements. It is evident that this regular increase of the perturbation constant with the mass number is a fundamental property of the nucleus and is unaffected by the external electronic structure which causes the inversion of the isotopic displacements in the transition from mercury (normal state $6s^2$) to lead ($6s^2.6p^2$). It would seem that the perturbation of the individual terms is due to a mutual sharing of identities by two valency electrons on account of their electrical interaction; for a given element this interaction might be affected by a change in some electrical property (e.g. the polarizability) of the nucleus from one isotope to the next, which would produce the observed slight differences in the perturbation constants. If the nuclei of the various isotopes are considered to be built up from that of the lightest isotope by the addition of neutrons, a systematic change in the polarizability of the nuclei so formed would be expected.

With regard to the ultimate cause of the isotopic displacements, it is interesting to note that the effect occurs almost exclusively in terms associated with configurations containing two equivalent valency electrons. The effect is most marked in those spectra where the resonance energy of such equivalent electrons is small, i.e. where the intercombination lines are strong. If the electrical interaction responsible for the Heisenberg-Dirac resonance energy were affected by the polarizability of the nucleus, then the term values of the various isotopes would show all the characteristic features of the displacement effect.

548.712:549.514.1

QUARTZ AS A STANDARD FOR ACCURATE LATTICE-SPACING MEASUREMENTS

By A. J. BRADLEY, Ph.D., Warren Research Fellow,

AND

A. H. JAY, M.Sc., Beyer Fellow of the University of Manchester

Communicated by Prof. W. L. Bragg, January 30, 1933.
Read April 7, 1933

ABSTRACT. A test has been made of the use of quartz as a standardizing substance for very accurate lattice-spacing determinations. With CuK_α radiation it gives a very good photograph with many sharp K_α doublets, which may be measured with accuracy. A redetermination of the axial ratio from an X-ray powder photograph gave

$$c/a = 1{\cdot}10002 \pm 0{\cdot}00004,$$

and this value was confirmed by X-ray measurements on several other crystals. Assuming Bergqvist's value for d_{100} (4246·02 X. units) we obtained $a = 4902{\cdot}9$ X., $c = 5393{\cdot}3$ X. Various specimens of quartz from different sources were compared by taking powder photographs in the same camera, one of the clear, colourless specimens being used to calibrate the camera, on the basis of the above values.

The values of d_{100} at 18° C. all lay between $4245{\cdot}9_5$ and 4246·30. The clear colourless crystals gave $4246{\cdot}0 \pm 0{\cdot}05$.

§ 1. INTRODUCTION

Although the value of the lattice spacing of a crystalline substance is usually expressed in Ångstrom units, and a high degree of accuracy may often be claimed for the measurements, such values are not absolute but only relative. The value of the Ångstrom is based on optical measurements, whereas lattice-spacing values are derived from X-ray wave-lengths which have not yet been accurately standardized. The latter were originally obtained from measurements on rock-salt and calcite, for which the lattice spacings had been deduced from a knowledge of the density and molecular weight with the help of calculations involving Avogadro's number, which in its turn depends upon the experimental determination of *e* by Millikan*. Thus the whole scale of wave-length values is *e*
influenced by the accuracy of the determination of *e*, and since this has not yet been made with a high degree of accuracy it has been impossible from crystal measurements to obtain X-ray wave-lengths of great accuracy on an absolute scale.

Attempts have been made to eliminate this difficulty by using methods to determine X-ray wave-lengths which do not involve the use of the Avogadro constant. The usual method is that of the ruled grating*. Probably the most accurate measurements are those of Backlin† and Cork‡, which, however, give values different from those determined from crystal measurements by an amount which exceeds experimental error. It therefore seems probable that the scale of wave-lengths is in error owing to an inaccuracy in the value of *e*. On the other hand the direct measurements are themselves not yet sufficiently accurate to warrant a change in wave-length standards. It is therefore customary to use, as an arbitrary X. standard, Siegbahn's values expressed in X units (X.), of which the latest series is given in the second edition of *Spektroskopie der Rontgenstrahlen*§.

---

* *Proc. Nat. Acad. Sci.* **3**, 314, (1917).

The object of our investigation was to find the most accurate means of basing powder-photographic determinations of lattice spacing on the Siegbahn scale of wave-lengths. In comparing the lattice spacing of a crystal with an X-ray wave-length, it is essential to measure the glancing angle of reflection. This may be found directly, but in X-ray powder photography greater accuracy is obtained if the instrument is first standardized by the use of a substance of known lattice spacing. The latter is either mixed with the material under investigation‖, or it may be used in a preliminary experiment in order to calibrate the instrument.

It is clearly an advantage to use for such a purpose a substance which has already been employed in the determination of wave-lengths by Siegbahn and his collaborators. Rock-salt was the first crystal to be used for wave-length measurements, but it has several serious disadvantages for powder photography, as well as for single-crystal measurements. It has been our experience that many samples of NaCl do not give sufficiently sharp reflections, and that there is a marked difference between the lattice spacings of different samples. This is in agreement with the work of Barth and Lunde¶, who have shown that the lattice spacing of chemically prepared NaCl is 5·626 Å., instead of 5·628 Å., which is the value universally assumed for natural rock-salt.

A suitable standard for use in X-ray powder photography must have a simple structure, and it should also have a low absorption coefficient for the radiation employed, in order to avoid the possibility of errors due to the displacement of lines by absorption. Of the substances other than rock-salt used in X-ray spectroscopy, we have found that calcite does not give very good photographs, probably on account of the high value of the primary extinction, and others, such as sugar and gypsum, give patterns that are much too complicated. After repeated trials we concluded that by far the best substance for the purpose was quartz. The present paper is an account of some experiments devised to test the suitability of quartz for the calibration of Debye-Scherrer cameras, where extreme accuracy might be desired.

---

* A. H. Compton and Doan, *Proc. Nat. Sci. U.S.A.* **11**, 598 (1925).

† *Dissert.* (Upsala, 1928); *Nature*, **125**, 239 (1930).

‡ *Phys. Rev.* **35**, 128 (1930).

§ Julius Springer, Berlin (1931).

‖ R. W. G. Wyckoff, *Z. Krist.* **59**, 55 (1923–4); Havighurst, Mack & Blake, *J. Amer. Chem. Soc.* **46**, 2368 (1924).

¶ *Zeit. f. Phys. Chem.* **126**, 417 (1927) also V. M. Goldschmidt, G.V. 8 (1927).

§ 2. DESCRIPTION OF CAMERA

In an earlier paper*, we have described a new method for the accurate determination of lattice spacings from Debye-Scherrer photographs. The film is placed round the circumference of the camera in the usual way (i.e. with the centre of the film corresponding to zero angle of reflection), but the ends of the exposed portion of the film are defined by means of two knife edges casting sharp shadows on the film†, as at *A*, *B* in figure 1 *a*. The knife edges are close to the point *X* where the incident beam enters the camera, allowing reflections to strike the film up to very large angles. The angular ranges *YA* and *YB* correspond approximately to 165°. The limitation is imposed in order to allow the slit system to reach almost to the centre of the camera.

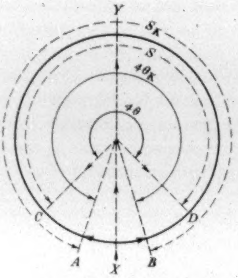


Figure 1 *a*. Illustrating method of calibration.

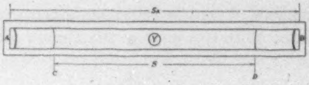


Figure 1 *b*.

When the film is unrolled, it has the appearance of figure 1 *b*, which is lettered to correspond with figure 1 *a*. The distance between the two knife edges S_k corresponds S_k to a definite angular range characteristic of the camera, θ_k. This is the only constant θ_k which has to be measured in order to calibrate the camera. However much the film shrinks,

$$\theta/\theta_k = S/S_k \qquad \text{......(1)},$$

where θ is the glancing angle of reflection corresponding to a distance S between the θ, S pair of lines in question. It is of course essential to measure S and S_k at the same time, as the film contracts and expands according to the state of the atmosphere.

It will be seen that the radius of the camera does not appear in equation (1). Also the lines at high angles, which give the spacing accurately, are in the neighbourhood of the standard shadow edges. The θ values from these lines are almost free from errors. The method has therefore all the advantages of the Van Arkel‡ arrangement in which film-shrinkage errors at high angles are avoided by placing the film back to front (i.e. with the incident beam passing through the centre of the film).

---

* *Proc. Phys. Soc.* **44**, 563 (1932).

† The use of knife edges for this purpose was adapted from the method employed by Phragmèn in his precision camera. See A. Westgren, *Trans. Amer. Inst. Mining and Met. Eng.* **31**, 13 (1931).

‡ A. E. van Arkel, *Physica*, **6**, 64 (1926).

The angle θ_k may be found from a direct measurement of the camera, but it is doubtful whether this gives an absolute accuracy of more than 1 part in 5000 in lattice spacing, since it is apt to introduce small errors which cannot be allowed for. For example, the shadows of the knife edges on the film may not coincide exactly with their calculated positions.

A much more accurate method of calibrating the camera is the use of a standard crystal, the spacings of which are accurately known. Errors in the camera constant are still introduced by this process of calibration, but they tend to cancel out when lattice spacings are being determined because every stage in the calibration process is repeated in the reverse direction. For example, no correction need be made for errors caused by the use of a beam of finite height, provided that this is the same in all experiments. Slight faults in the construction of the camera do not matter in this method.

Errors due to centring, absorption, and film shrinkage, which vary in amount from one photograph to another, require individual treatment. However, as we have shown, the ratio S/S_k makes complete allowance for film shrinkage. The method of eliminating errors due to centring in the process of calibration is described later. With this method the camera constant may be obtained correct to about 1 part in 15,000, which is sufficient to give lattice spacings with an accuracy of about 1 part in 50,000 *relative to the chosen standard.*

§ 3. METHOD OF CALIBRATING CAMERA

The (100) spacing of quartz has been accurately determined by Bergqvist*, who used CuK radiation. The same radiation was employed in our experiments, so
d that there was no doubt about the accuracy of the (100) spacing d in terms of the wave-length.

Bergqvist gives:

for $K\alpha_1$, λ = 1537·395 X.
for $K\alpha_2$, λ = 1541·232 X.
for quartz, d = 4246·02 X. at 18° C.

after correcting for the refractive index.

In Bergqvist's measurements the refractive index produced a considerable deviation from the simple law of X-ray reflection

$$n\lambda = 2d \sin\theta,$$

since he used the lowest orders of reflection. We worked only at high angles, where the effect was much less important, requiring only a small correction.

c The c spacing of quartz was calculated from an assumed value of the axial
a ratio. Groth† gives $a : c = 1{\cdot}0999$, as found by Kupfer‡ in 1825§. Combining this

---

[*] O. Bergqvist, *Z. f. Phys.* **66**, 494 (1930).

[†] *Chemische Kristallographie*, **1**, p. 86.

[‡] *Preisschr. d. Akad. d. Wissensch.* **61** (Berlin, 1825).

[§] A later determination by Tutton (*Crystallography*, p. 373) gives 1·1000.

with Bergqvist's value, we obtain for the axes $a = 4902{\cdot}88$ X.; $c = 5392{\cdot}68$ X. at 18° C.*

The c value cannot be exact, but it is accurate enough to fix the indices of the observed reflections. A very accurate determination of the axial ratio is made in the present paper, but at the beginning of the work the exact value was unknown.

The problem was to calibrate the camera, i.e. to find θ_k, without an accurate knowledge of c/a, and at the same time eliminate errors due to the centring of the specimen.

The use of a thin diluted specimen of quartz with CuK$_\alpha$ radiation eliminates absorption errors, but it is almost impossible to ensure that the specimen is exactly at the centre of the camera. This causes a systematic displacement of the lines on the film, which has a far greater effect at low than at high angles. In our former paper it was shown that accurate lattice-spacing determinations could be made by plotting the spacing values from individual lines against the corresponding values of $\cos^2 \theta$, and extrapolating a linear curve through the points to $\cos^2 \theta = 0$†. This method must be slightly modified in order to determine θ_k, as the following considerations will show. From our earlier paper, the error dS in the measured distance between dS
corresponding lines is given by:

$$ds = -2 . p \cos \phi . \sin 2\theta \qquad \text{......(2)}$$

where p is the displacement of the specimen from the centre of the camera and ϕ is p, ϕ
the direction of displacement measured from the direction of incidence. The error dS causes an error $d\theta_k$ in θ_k which is given by $d\theta_k$

$$\frac{d\theta_k}{\theta_k} = -\frac{dS}{S} = \frac{p \cos \phi}{R} \frac{\sin 2\theta}{2\theta} \qquad \text{......(3),}$$

R being the radius of the camera. R

Equation 3 shows that the value of $d\theta_k$ varies linearly with $\sin 2\theta/2\theta$, falling to zero when $\sin 2\theta/2\theta = 0$, and $\theta = 90°$. If, therefore, the values of θ_k obtained from different lines be plotted against the corresponding values of $\sin 2\theta/2\theta$ a straight line should be obtained, and if this line be extrapolated to $\sin 2\theta/2\theta = 0$, the correct value of θ_k should be found, with a complete elimination of the errors caused by centring.

In practice the presence of individual errors of measurement prevents the values of θ_k from lying exactly on a straight line. They should, however, be grouped on either side of a straight line in a random manner if c and a are correct. If, however, an incorrect axial ration has been assumed, so that while a is correct c is in error, this will be shown by a systematic deviation of points corresponding to different sets of indices from a mean line. If, for example, the ratio c/a has been given too small a value, points for large values of l will fall above the mean line, the departure being greater the greater the value of l. A new value of the axial ratio must be found which brings all the points on to the same line, apart from random errors of measurement.

---

* W. Zachariasen, *Z. Krist.* **67**, 226 (1927), gives $a = 4{\cdot}903$ Å., $c = 5{\cdot}393$ Å., $c/a = 1{\cdot}0999$.

† An extrapolation method was first used by Kettmann, *Z. f. Phys.* **53**, 198 (1929), who plotted the lattice-spacing values for individual lines against their θ values. However, since this curve turns over rapidly towards $\theta = 90°$ it allows considerable latitude in the interpretation of the results.

To sum up, the θ_k values found by applying equation (1) to each line on the film may be in error for two reasons. (i) The measured value of s may have systematic errors due to the eccentricity of the specimen in the camera. (ii) The calculated values of θ may have systematic errors due to inaccuracy of the axial ratio. These effects may be eliminated by the following procedure. (1) Plot the values of θ_k against the corresponding values of $\sin 2\theta/2\theta$. (2) Observe whether there is a systematic deviation of points about a mean straight line for planes with large and small values of l. Such an effect indicates an error in the axial ratio. (3) By a process of trial and error, find a value of the axial ratio which brings points for large and small values of l upon the same curve. (4) Estimate the camera constant θ_k by extrapolation to $\sin 2\theta/2\theta = 0$.

§4. LIMITS OF ACCURACY

The accuracy of the determination of θ_k depends upon the validity of the method for eliminating systematic errors, and on the accuracy of individual measurements. The former depends upon the absence of errors due to causes other than centring, while the latter depends on the intensity-distribution across the lines and on the measuring instrument.

In our experiments a camera of diameter 9 cm. was calibrated by means of a powder photograph taken with CuK_α radiation. β lines were eliminated by means of a nickel screen. The specimen was obtained by grinding up a crystal of pure quartz, which was mixed with about three times its own volume of Canada balsam and mounted on a hair at the centre of the camera, in the form of a cylinder 0·4 mm. in diameter. The displacement of the lines due to absorption of the Cu radiation by the specimen is almost eliminated by this procedure. Continual rotation of the specimen and a special slit system yield strong lines of symmetrical shape, with sharply defined peaks, which correspond closely to the centre of gravity of the lines.

A reproduction of one side of the quartz film is shown in figure 2*a*. Figure 2*b* shows an enlargement of the portion containing the resolved K_α doublets. Near the end of the film the doublets are sufficiently separated for the measurements to be uninfluenced by overlapping, and a very high accuracy can then be attained. To test the possible accuracy, photometer readings were obtained from the doublet for which $h\,k\,l = 2\;3\;4$. The microphotometer curve for this line is given in figure 3*a*, for which readings were taken at intervals of 0·01 cm. It is clear from this curve that the position of the peaks is not influenced by the presence of neighbouring lines.

An attempt was then made to find how accurately the position of the peak could be measured. The portions *AB*, *CD* at the summits of the curves, which were examined in detail, are reproduced in figure 3*b*. The readings were taken at intervals of 0·001 cm. It appears from these curves that the peaks may be measured to ± 0·0001 cm. This degree of accuracy is far beyond our requirements, and in practice measurements are made with a travelling microscope reading to 0·001 cm.

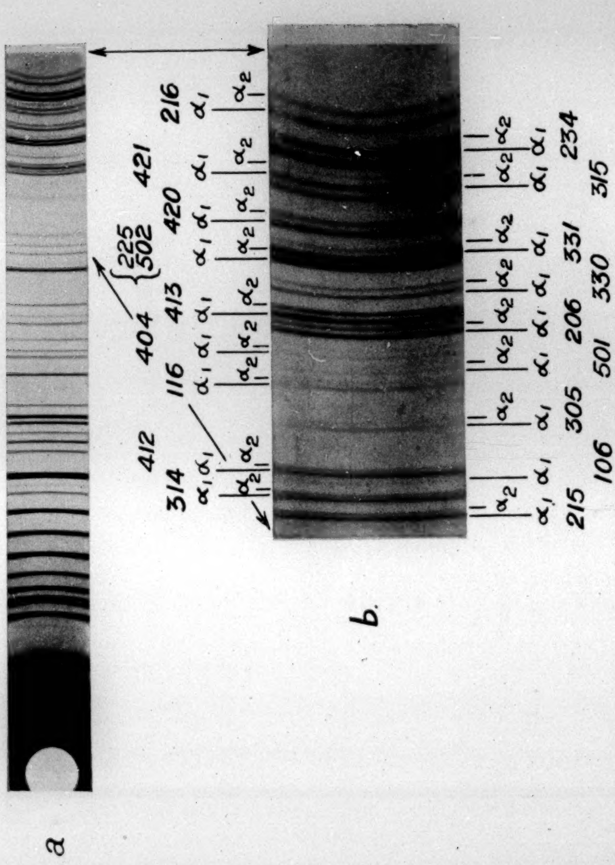

a
b
216
421
420
225
502
404
413
116
412
314
α1
α2
234
315
331
330
206
501
305
106
215

Figure 2. Powder photographs of quartz.

The limit of accuracy is then of the order of 0·001 cm. to 0·003 cm. for the distance between a pair of corresponding lines. This corresponds to an accuracy between about 1 part in 25,000 and 1 part in 10,000 in determining θ.

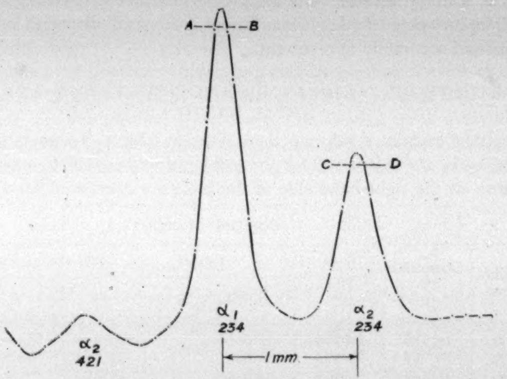
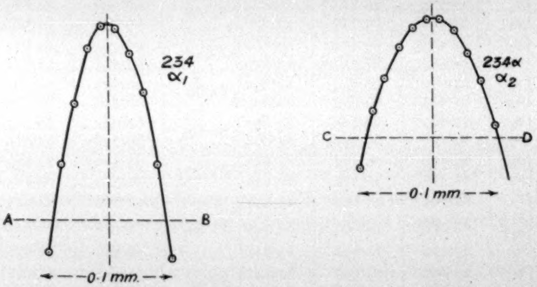


Figure 3*a*. Photometer curves of quartz.



(*Mean bisector* 0·9185 ± 0·0001 *cm.*) (*Mean bisector* 0·8186 ± 0·0001 *cm.*)

Figure 3*b*. ⊙ Photometer readings at intervals of 0·01 mm.

This high accuracy can only be attained in the case of strong lines near the end of the film where the doublets are well resolved. The other lines are less reliable and are only used as pointers, whereas the accurate lines serve as pivots for the extrapolation curve. It should be possible with one or two accurate doublets and a large number of pointers to obtain the value of θ_k to at least one part in 15,000.

Everything depends on the high angle lines. These must be close to the knife edges, and the film must be pressed down flat at this point. To ensure this, the ends of the film are slipped under a steel plate which holds them down firmly against the circumference of the camera. It is not essential to avoid errors which influence only the lines at low angles. For example, if the film bulges slightly near the centre, both S and S_k are increased somewhat, but for the high angle measurements the ratio of S to S_k is scarcely affected. The measuring instrument need not be absolutely accurate along its whole length. It is sufficient if the small distances between S and S_k are measured accurately to 0·001 cm.

§5. RESULTS OF CALIBRATION AND REDETERMINATION OF AXIAL RATIO

Two series of calculated values of θ are given in table 1. Those on the left-hand side of the table are calculated for an axial ratio c/a equal to 1·0999 (Groth's value). Those on the right-hand side of the table are calculated for an axial ratio

Table 1. Calibration of camera 1

h, k, l	Radiation	Observed S (cm.)	Axial ratio c/a = 1·0999			Axial ratio c/a = 1·10002		
			θ*	θ_k or $\theta S_k/S$		θ*	θ_k or $\theta S_k/S$	
412	α_1	19·556	61·313	82·906	82·89	61·312	82·905	82·89
	α_2	19·652	61·575	82·854		61·574	82·852	
305	α_1	20·301	63·648	82·905	$82{\cdot}90_5$	63·640	82·894	82·89
	α_2	20·395	63·938	82·899		63·930	82·888	
116	α_1	20·937	65·636	82·898	$82{\cdot}89_5$	65·624	82·882	$82{\cdot}87_5$
	α_2	21·042	65·954	82·884		65·942	82·868	
501	α_1	21·184	66·400	82·885	$82{\cdot}88_5$	66·399	82·883	$82{\cdot}88_5$
	α_2	21·288	66·729	82·888		66·729	82·888	
404	α_1	21·432	67·175	82·882	82·88	67·169	82·874	$82{\cdot}87_5$
	α_2	21·542	67·517	82·879		67·511	82·871	
206	α_1	21·770	68·243	82·892	82·89	68·229	82·874	$82{\cdot}87_5$
	α_2	21·885	68·603	82·892		68·590	82·874	
413	α_1	22·007	68·965	82·867	$82{\cdot}86_5$	68·961	82·862	82·86
	α_2	22·127	69·340	82·866		69·336	82·860	
330	α_1	22·396	70·173	82·853	82·85	70·173	82·853	82·85
	α_2	22·527	70·573	82·841		70·573	82·841	
502 225	α_1	22·868	71·650	82·851	$82{\cdot}84_5$	71·646	82·847	$82{\cdot}84_5$
	α_2 α_1	23·007	72·080	82·845		72·078	82·843	
331	α_2	23·150	72·522	82·838		72·522	82·838	
420	α_1	23·407	73·332	82·843	82·84	73·332	82·843	82·84
	α_2	23·563	73·816	82·838		73·816	82·838	
315	α_1	23·977	75·122	82·848	$82{\cdot}84_5$	75·109	82·834	82·84
	α_2 α_1	24·138	75·629	82·851		75·622	82·843	
421	α_2	24·310	76·154	82·836		76·154	82·836	
234	α_1	24·517	76·799	82·832	$82{\cdot}82_9$	76·790	82·822	$82{\cdot}81_9$
	α_2	24·719	77·423	82·823		77·413	82·812	
216	α_1	25·088	78·600	82·845	$82{\cdot}84_2$	78·576	82·820	$82{\cdot}81_7$
	α_2	25·324	79·332	82·837		79·307	82·811	
End of film:		26·443 (S_k)						

Extrapolated value for $\theta_k = 82{\cdot}77°$, c/a being taken as 1·10002.

* Values of θ calculated from Bergqvist's d value with correction for refraction.

1·10002, which will be shown to be more nearly correct. For overlapping lines an estimated value depending on the relative intensities of the component parts is given for θ. The value of θ_k for each line was determined from θ, S, and S_k by means of equation (1); values for each line are shown in table 1.

A weighted mean was found for θ_k from each pair of K_α doublets by giving α_1 twice the weight of α_2.

The presence of systematic errors was tested by plotting the values of θ_k from table 1 against $\sin 2\theta/2\theta$ in figure 4*a*. The values deduced, an axial ratio $c/a = 1{\cdot}0999$ being assumed, are represented by crosses. The crosses show a gradual fall as $\sin 2\theta/2\theta$ falls, indicating that the specimen was incorrectly centred. However, they do not lie at random about a straight line but are distributed in a regular fashion.

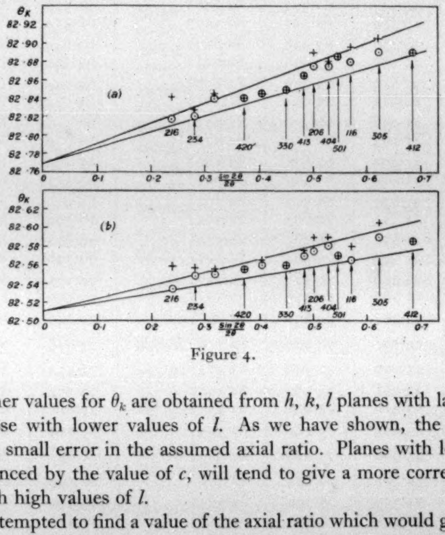


Figure 4.

Relatively higher values for θ_k are obtained from h, k, l planes with large values of l than from those with lower values of l. As we have shown, the effect may be explained by a small error in the assumed axial ratio. Planes with low values of l, being uninfluenced by the value of c, will tend to give a more correct value for θ_k than those with high values of l.

We have attempted to find a value of the axial ratio which would give no systematic variation in θ_k for high and low l indices. By trial and error the axial ratio 1·10002 was found to satisfy this condition. In figure 4*a* the revised axial ratio gives the values of θ_k indicated by circles. These circles are distributed roughly within an acute triangle, the apex of which lies at $\sin 2\theta/2\theta = 0$, $\theta = 90°$. The downward slope from right to left is due to a systematic eccentricity error. The deviation of the circles from a straight line is due to individual errors of measurement, which are greatest at the lowest angles. By extrapolation to $\sin 2\theta/2\theta = 0$ it is seen that the most probable value of θ_k for this camera is 82·77° with a probable error of not more than 0·005°.

If the method were sound it should be possible by repeating the process in another camera to obtain the same value for the axial ratio. The results of this experiment are shown in table 2 and figure 4*b*. The θ_k values represented by crosses are calculated for $c/a = 1{\cdot}0999$, and show the same systematic deviation as in the upper figure. The circles for $c/a = 1{\cdot}10002$ are much more consistent, and it therefore seems probable that this is the true value for the axial ratio. By extrapolation we get 82·51° for the most probable value of θ_k for the second camera.

Table 2. Calibration of camera 2

h, k, l	Radiation	Observed S (cm.)	Axial ratio $c/a = 1{\cdot}0999$			Axial ratio $c/a = 1{\cdot}10002$		
			θ*	θ_k or $\theta S_k/S$		θ*	θ_k or $\theta S_k/S$	
412	α_1 α_2	19·437 19·534	61·313 61·575	82·606 82·547	82·58$_5$	61·312 61·574	82·605 82·546	82·58$_5$
305	α_1 α_2	20·178 20·270	63·648 63·938	82·603 82·603	82·60$_5$	63·640 63·930	82·592 82·592	82·59
116	α_1 α_2	20·815 20·912	65·636 65·954	82·576 82·591	82·58	65·624 65·942	82·561 82·576	82·56$_5$
501	α_1 α_2	21·058 21·163	66·400 66·729	82·573 82·571	82·57	66·399 66·729	82·571 82·570	82·57
404	α_1 α_2	21·302 21·404	67·175 67·517	82·580 82·605	82·59	67·169 67·511	82·572 82·597	82·58
206	α_1 α_2	21·637 21·754	68·243 68·603	82·594 82·584	82·59	68·229 68·590	82·577 82·567	82·57$_5$
413	α_1 α_2	21·870 21·992	68·965 69·340	82·579 82·567	82·57$_5$	68·961 69·336	82·573 82·562	82·57
330	α_1 α_2	22·259 22·382	70·173 70·573	82·556 82·571	82·56	70·173 70·573	82·556 82·570	82·56
502 225	α_1	22·724	71·650	82·568	82·56$_5$	71·646	82·564	82·56
	α_2 α_1	22·864	72·080	82·556		72·078	82·554	
331	α_2	23·000	72·522	82·571		72·522	82·571	
420	α_1 α_2	23·261 23·416	73·332 73·816	82·556 82·551	82·55$_5$	73·332 73·816	82·556 82·551	82·55$_5$
315	α_1	23·829	75·122	82·555	82·55$_5$	75·109	82·541	82·55
	α_2 α_1	23·986	75·629	82·569		75·622	82·561	
421	α_2	24·161	76·154	82·540		76·154	82·540	
234	α_1 α_2	24·359 24·561	76·799 77·423	82·562 82·548	82·55$_7$	76·790 77·413	82·553 82·538	82·54$_8$
216	α_1 α_2	24·931 25·164	78·600 79·332	82·560 82·557	82·55$_9$	78·576 79·307	82·535 82·531	82·53$_4$
End of film:		26·187 (S_k)						

Extrapolated value for $\theta_k = 82{\cdot}51°$, using $c/a = 1{\cdot}10002$.

* Values of θ calculated from Bergqvist's d value with correction for refraction.

The axial ratio of quartz is much nearer 1·10002 *than* 1·0999. We now have the following values:

$a = 4902{\cdot}88$ X. (calculated from Bergqvist)

$c = 5393{\cdot}27 \pm 0{\cdot}1$ X.

$c/a = 1{\cdot}10002 \pm 0{\cdot}00004$.

§6. EXPERIMENTS WITH OTHER SPECIMENS OF QUARTZ

The above data are valid for the particular specimen of quartz used in our calibration experiments. It was interesting to see whether the same values would be obtained from other specimens. One of the cameras calibrated in the above experiments was used to take photographs from a number of different quartz crystals, the temperature being maintained at 18° during each exposure.

Table 3. Clear quartz (Cornwall)

h, *k*, *l*	Radiation	S (cm.)	θ (degrees)	Lattice spacing of 100 planes (X.)	
305	α_1	20·220	63·632	4246·3	4246·3
	α_2	20·314	63·927	·2	
116	α_1	20·848	65·608	4246·6	4246·4
	α_2	20·953	65·938	·2	
206	α_1	21·678	68·220	4246·3	4246·4
	α_2	21·791	68·575	·5	
413	α_1	21·909	68·947	4246·4	4246·3
	α_2	22·031	69·331	·2	
330	α_1	22·297	70·168	4246·1$_5$	4246·2
	α_2	22·422	70·561	·4	
502 225	α_1	22·763	71·634	4246·3	4246·3
	α_2 α_1	22·900	72·065	·3	
331	α_2	23·043	72·515	·2	
420	α_1	23·300	73·324	4246·2	4246·2
	α_2	23·454	73·809	·1$_5$	
315	α_1	23·864	75·099	4246·2	4246·2
	α_2 α_1	24·026	75·609	·2$_5$	
421	α_2	24·200	76·156	·0	
234	α_1	24·399	76·783	4246·1	4246·1$_5$
	α_2	24·596	77·403	·2	
216	α_1	24·966	78·567	4246·1$_5$	4246·1
	α_2	25·200	79·303	·0$_5$	
End of film:		26·219 (S_k)	82·51 (θ_k)		

Extrapolated values of d_{100}: 4246·0$_5$ ± 0·05 X.

The experiments fall into two groups. First two clear crystals were examined, and the results are given in tables 3 and 4, and in figures 5*a* and *b*. The tables show the measured values of S with the values of θ deduced from them, and for each line a value of the lattice spacing is calculated from them. To eliminate systematic errors the procedure described in our earlier paper was used. A value of the lattice spacing is deduced for each line, and the weighted mean for each K_α doublet is then plotted against the appropriate value of $\cos^2\theta$. The points should lie near a straight line, which gives the correct value of the lattice spacing by extrapolation to $\cos^2\theta = 0$. This method is directly applicable only to cubic crystals, where there is only one variable. For hexagonal crystals, where there are two variables *a* and *c*, one of these

Table 4. Clear quartz (St Gothard)

h, k, l	Radiation	*S* (cm.)	θ (degrees)	Lattice spacing of 100 planes (X.)	
305	α_1	20·203	63·619	4246·8	4246·8
	α_2	20·296	63·912	·7	
116	α_1	20·835	65·608	4246·6	4246·6
	α_2	20·934	65·921	·7	
206	α_1	21·659	68·204	4246·7	4246·7
	α_2	21·775	68·569	·6	
413	α_1	21·894	68·944	4246·5	4246·6
	α_2	22·011	69·313	·7	
330	α_1	22·281	70·163	4246·3	4246·3
	α_2	22·406	70·556	·4	
502 225	α_1	22·745	71·624	4246·6	4246·4
	α_2 α_1	22·887	72·071	·2	
331	α_2	23·027	72·512	·2	
420	α_1	23·284	73·321	4246·2$_5$	4246·2$_5$
	α_2	23·438	73·806	·2$_5$	
315	α_1	23·848	75·097	4246·2$_5$	4246·3
	α_2 α_1	24·010	75·607	·3	
421	α_2	24·177	76·113	·4	
234	α_1	24·382	76·779	4246·2	4246·2
	α_2	24·581	77·405	·1$_5$	
216	α_1	24·950	78·567	4246·1$_5$	4246·1
	α_2	25·174	79·304	·0$_5$	
End of film:		26·202 (S_k)	82·51 (θ_k)		

Extrapolated value of d_{100}: 4245·9$_5$ ± 0·05 X.

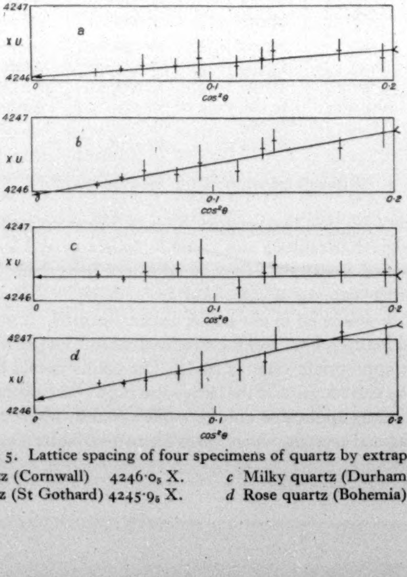


Figure 5. Lattice spacing of four specimens of quartz by extrapolation.

a Clear quartz (Cornwall) 4246·0$_5$ X. *c* Milky quartz (Durham) 4246·3$_0$ X.
b Clear quartz (St Gothard) 4245·9$_5$ X. *d* Rose quartz (Bohemia) 4246·2$_0$ X.

must be eliminated before the graphical method is applied. To this end we assume a value for the axial ratio and determine the (100) spacing for each line.

In the present experiments we assumed that $c/a = 1{\cdot}10002$, and deduced a value of the spacing for each line. In figure 5 the weighted mean for each doublet is plotted against the appropriate value of $\cos^2\theta$. The probable accuracy of each value is indicated by the length of the line. There is no systematic deviation of points for planes with different values of l, which would if present show that the axial ratio was incorrect. It may be concluded that the axial ratio of the two new specimens of quartz is 1·10002 as in the former experiment. The points lie very close to a straight line, which, on extrapolation, gives for d_{100} the value $4246{\cdot}0_5 \pm 0{\cdot}05$ X. and $4245{\cdot}9_5 \pm 0{\cdot}05$ X. respectively, proving that the lattice spacing of quartz is identical in the three *clear* crystals examined to within 1 part in 50,000.

Table 5. Milky quartz (Durham)

h, k, l	Radiation	S (cm.)	θ (degrees)	Lattice spacing of 100 planes (X.)	
305	α_1	20·221	63·627	4246·5	4246·4
	α_2	20·315	63·923	·3	
116	α_1	20·853	65·616	4246·3	4246·4
	α_2	20·951	65·924	·6	
206	α_1	21·679	68·215	4246·5	4246·5
	α_2	21·793	68·574	·5	
413	α_1	21·912	68·948	4246·4	4246·4
	α_2	22·032	69·326	·3	
330	α_1	22·299	70·166	4246·2	4246·3
	α_2	22·421	70·550	·6	
502 225	α_1	22·763	71·626	4246·5	4246·6
	α_2 α_1	22·899	72·054	·6	
331	α_2	23·039	72·494	$\cdot 6_5$	
420	α_1	23·300	73·316	4246·4	$4246{\cdot}4_5$
	α_2	23·451	73·791	$\cdot 5_5$	
315	α_1	23·864	75·090	4246·4	4246·4
	α_2 α_1	24·028	75·606	$\cdot 3_5$	
421	α_2	24·194	76·129	$\cdot 4_5$	
234	α_1	24·398	76·771	$4246{\cdot}3_5$	4246·3
	α_2	24·599	77·403	·2	
216	α_1	24·965	78·555	$4246{\cdot}3_5$	$4246{\cdot}3_5$
	α_2	25·197	79·285	$\cdot 3_5$	
End of film:		26·222 (S_k)	82·51 (θ_k)		

Extrapolated value of d_{100}: $4246{\cdot}3_0 \pm 0{\cdot}05$ X.

Further experiments were made with cloudy and coloured specimens. The results of two experiments with milky and coloured crystals respectively are given in tables 5 and 6 and in figures 5*c* and 5*d*. The following values were obtained:

For milky quartz $d_{100} = 4246{\cdot}3_0 \pm 0{\cdot}05$ X.

For rose quartz $d_{100} = 4246{\cdot}2_0 \pm 0{\cdot}05$ X.

The increase in spacing, though not great, definitely exceeds the experimental error. In experiments with crystals which were less uniformly or less distinctively marked a smaller increase in spacing was found. In no instance was there any indication of a different axial ratio.

Table 6. Rose quartz (Bohemia)

h, k, l	Radiation	S (cm.)	θ (degrees)	Lattice spacing of 100 planes (X.)	
395	α_1	20·197	63·610	4247·1	4247·0
	α_2	20·293	63·912	6·7	
116	α_1	20·825	65·587	4247·2	4247·1
	α_2	20·927	65·909	·0	
206	α_1	21·653	68·195	4247·0	4247·0
	α_2	21·767	68·554	·0	
413	α_1	21·887	68·933	4246·8	4246·7
	α_2	22·010	69·320	·4	
330	α_1	22·272	70·145	4246·7	4246·6
	α_2	22·403	70·558	·4	
502 225	α_1	22·739	71·616	4246·7	4246·6
	α_2 α_1	22·879	72·056	·5	
331	α_2	23·021	72·504	·4	
420	α_1	23·276	73·307	$4246{\cdot}5_5$	$4246{\cdot}5_5$
	α_2	23·430	73·792	$\cdot 5_5$	
315	α_1	23·842	75·090	4246·4	$4246{\cdot}4_5$
	α_2 α_1	24·005	75·603	·4	
421	α_2	24·169	76·120	·6	
234	α_1	24·375	76·769	4246·4	4246·4
	α_2	24·573	77·392	$\cdot 3_5$	
216	α_1	24·941	78·551	4246·4	4246·4
	α_2	25·174	79·285	$\cdot 3_5$	
End of film:		26·198 (S_k)	82·51 (θ_k)		

Extrapolated value of d_{100}: $4246{\cdot}2_0 \pm 0{\cdot}05$ X.

§7. CONCLUSIONS

Our experiments have shown that quartz is a very suitable substance to use for the calibration of powder photograph cameras when this operation is performed in a preliminary experiment. It would scarcely be possible to use quartz in the mixture method owing to the large number of lines in the X-ray pattern. It has, however, been shown that by the authors' methods an accuracy of 1 part in 50,000 may be attained without mixing the powders.

Quartz gives with CuK_α radiation an extremely good powder photograph in which the K_α doublets at high angles may be clearly resolved and accurately measured. For convenience of reference the glancing angles of reflection θ for these lines are given in table 7, together with sin $2\theta/2\theta$ which is required for the extrapolation process. The values given in this table are corrected for deviation from Bragg's law.

In the case of overlapping lines we have made an estimate of the angle corresponding to the centre of gravity of the reflection.

Table 7. Glancing angles for quartz, on the assumption that $a = 4902{\cdot}88$ X., $c = 5393{\cdot}27$ X.

h, k, l	Radiation	θ*	$\sin 2\theta/2\theta$
216	α_2	79·307	0·238
	α_1	78·576	
234	α_2	77·413	0·282
	α_1	76·790	
421	α_2	76·154	0·319
	α_1 α_2	75·622	
315	α_1	75·109	
420	α_2	73·816	0·371
	α_1	73·332	
331	α_2	72·522	0·406
	α_1 α_2	72·078	
225 502	α_1	71·646	
330	α_2	70·573	0·451
	α_1	70·173	
413	α_2	69·336	0·483
	α_1	68·961	
206	α_2	68·590	0·501
	α_1	68·229	
404	α_2	67·511	0·530
	α_1	67·169	
501	α_2	66·729	0·549
	α_1	66·399	
116	α_2	65·942	0·571
	α_1	65·624	
305	α_2	63·930	0·623
	α_1	63·640	
412	α_2	61·574	0·685
	α_1	61·312	

* Corrected for refractivity.

Smoky and coloured crystals have a slightly larger spacing, and must be avoided for calibration work. Our results are not in agreement with a paper recently published by Yuchting Tu*. In an investigation of the lattice spacing of quartz he finds that the measurements from different faces of the same form (i.e. different 101 faces or different 100 faces) on the same crystal vary by as much as 1 per cent. For this reason he thinks that quartz is unsuitable as a standard for wave-length determinations. Yuchting Tu states that his crystals appear to be distorted. This is the probable explanation of the discrepancies. In our experiments only good crystals with smooth faces were used. Among 10 such crystals, all from different localities, we did not find one which failed to resolve the α doublets clearly and distinctly, which would be impossible with variations of the order of 1 per cent. Moreover, in every case the measurements from different planes were consistent within the limits of experimental error; this is well shown by figure 5. The four examples selected in this diagram include the *biggest* differences in lattice spacing out of the 10 specimens measured.

---

* *Phys. Rev.* **40**, 662 (1932).

In conclusion we give a summary of the steps in our method of lattice-spacing determination. (*a*) *Calibration of the camera.* An angle θ_k characteristic of the camera is found from a powder photograph of quartz by means of equation (3) and the values of θ in table 7. If the values of θ_k from different lines show a systematic divergence, they are plotted against $\sin 2\theta/2\theta$ and extrapolated to $\sin 2\theta/2\theta = 0$, (*b*) *Calculation of the glancing angles* for any substance, from powder photograph measurements and the camera constant θ_k. (*c*) *Deduction of lattice spacing.* From each θ value the lattice spacing is deduced. If the crystal is hexagonal, trigonal or tetragonal* an approximate value of the axial ratio is assumed and only one of the lattice spacings (d) is found for each line. The value of d for each α doublet is then plotted against the appropriate value of $\cos^2\theta$ and the points are extrapolated to $\cos^2\theta = 0$. This gives the most probable value of the lattice spacing. If the values of d show a systematic divergence from a straight line the axial ratio is incorrect and must be adjusted. It is, however, important to confine measurements as far as possible to values of θ between 60° and 90° for accurate work.

By the above methods it is possible to obtain very accurate values of lattice spacings from photographs in circular cameras of diameter 9 cm. This has the advantage of requiring only a short time of exposure, and moreover a complete powder photograph which may be useful for other purposes is obtained at the same time as the accurate lattice-spacing determination.

§8. ACKNOWLEDGMENTS

In conclusion we desire to thank Professor W. L. Bragg, F.R.S., for his encouraging interest in the work, which was carried out in the Physical Laboratories of the University of Manchester. We also thank Mr A. P. M. Fleming, C.B.E., Director-Manager, Research and Education Departments of the Metropolitan-Vickers Elec. Co. Ltd., for his kind and helpful interest. We are indebted to Dr H. E. Buckley and Dr J. W. Jackson for the specimens of quartz.

---

* The method may be extended to orthorhombic crystals where the approximate values of the axial ratios are known.

536.222:546.212

THE THERMAL CONDUCTIVITY OF WATER

By L. H. MARTIN, Ph.D., and K. C. LANG, M.A., M.Sc.,
University of Melbourne

Communicated by Prof. T. H. Laby, January 1, 1933. Read April 7, 1933

ABSTRACT. The paper describes the precise measurement of the thermal conductivity of water in a range of temperatures extending from 7° C. to 60° C. The parallel-plate method has been employed, the apparatus being especially designed to cope with the difficulties which arise in the measurement of the conductivity of a volatile liquid. Two series of measurements were made, the plates in one apparatus having approximately three times the area of those in the other.

§ 1. PREVIOUS MEASUREMENTS

In the past the hot-wire method and the parallel-plate method have been used to measure the conductivity of liquids. The use of the first has been confined principally to relative measurements as very narrow tubes must be employed to prevent convection and it is (Goldschmidt)* impossible to determine with sufficient accuracy the geometry of the apparatus. In previous plate experiments the corrections applied have usually been considerable, and the results obtained do not agree within the limits of the claimed accuracy of the separate measurements.

The work previous to 1920 has been critically discussed by Jacob†. Notable among these early experiments is that of Lees‡, who developed the plate method and found, by means of it, that water possessed a relatively large negative temperature coefficient of thermal conductivity. Jacob himself carried out an extensive series of measurements and obtained definite evidence of a positive coefficient. This result has since been confirmed by Bridgman§, Davis‖, and Kay and Higgins¶, but the actual magnitude of the coefficient still remains uncertain, the values found lying within the range 0·001 to 0·003. A similar lack of agreement exists in the values given to the conductivity at 0° C. These range from $1{\cdot}32 \times 10^{-3}$ to $1{\cdot}45 \times 10^{-3}$ cal./sec.-deg.-cm. It is possible that this lack of agreement is due in part to the fact that, with the exception of Jacob's experiments, the investigations on water have been incidental to other problems. In view of the fundamental importance of water, both from the point of view of theory and practice, the authors felt that further work on it was justified.

---

* *Phys. Z.* **12**, 417 (1911).

† *Ann. d. Phys.* 4, **63**, 537 (1920).

‡ *Phil. Trans.* A, **191**, 399 (1898).

§ *Proc. Nat. Acad. Sci.* **9**, 341 (1923).

‖ *Phil. Mag.* **47**, 1057 (1924).

¶ *Proc. R. S.* A, **117**, 459 (1928).

§2. PRINCIPLE OF THE METHOD

A film of water is formed between two parallel plates, the bottom one being held at a constant temperature by water-circulation while the upper one is heated electrically. Since the upper plate is hotter than the lower there can be no convection, provided the film is horizontal. Loss of heat by the top plate to the surroundings is prevented by a guard dome, which is maintained at a slightly higher temperature than the top plate.

Assuming a normal flow of heat through the water film from the electrically heated top plate to the bottom plate,

$$E_1E_2/JR = k.A.\Delta\theta/2a + L + E,$$

where

E_1 E_1 is the p.d. across the heating coil;
E_2, R E_2 the p.d. across a standard series resistance R;
k k cal./sec.-deg.-cm. the coefficient of thermal conductivity;
A A the area of each plate;
L L the rate of loss of heat to the surroundings;
E E the rate at which heat is used in the evaporation of water; and
$\Delta\theta/2a$ the temperature-gradient in the film.

On account of evaporation, especially at the higher temperatures, it is difficult to maintain the free surface of the liquid perpendicular to the plates. A calculation was therefore made of the effect of curved edges to the film. Suppose $ABCD$, figure 1, to be a vertical diametral section of the liquid film, the section AB of the
a free surface being part of a circle of radius R. The thickness of the film is $2a$, the
r diameter of the plates $2r$.

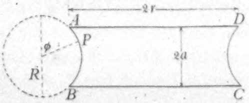


Figure 1.

Consider the heat-flow across a section of the film parallel to the plates through any point P. Assuming that there is no lateral heat-loss the equation of the heat-flow is

$$\frac{\partial}{\partial x}\left(sk\frac{\partial\theta}{\partial x}\right) = 0 \qquad \text{......(1),}$$

θ, x, s where θ is the temperature at a distance x from the top plate and s is the area of the section.

This gives $$sk/R\sin\phi = Q\,\partial\phi/\partial\theta \qquad \text{......(2),}$$

Q where Q calories is the quantity of heat passing any section per second.

Hence $$k\frac{\partial\theta}{\partial\phi} = \frac{QR\sin\phi}{\pi\{r - R\sin\phi + \sqrt{(R^2 - a^2)}\}}$$

and $$\pi k\Delta\theta = \frac{2a.b.Q}{r(b^2 - R^2)} + \frac{2R^2Q}{(b^2 - R^2)^{\frac{3}{2}}}\tan^{-1}\frac{a\sqrt{(b^2 - R^2)}}{b\sqrt{(R^2 - a^2)} - R^2} \qquad \text{......(3),}$$

where $\Delta\theta$ is the temperature-difference between the plates and $b = r + \sqrt{(R^2 - a^2)}$. $\Delta\theta$
For a straight edge ($R \rightarrow \infty$) this becomes

$$\pi k \Delta\theta = 2aQ/r^2. \qquad \text{......(4).}$$

This is the expression used for k when the curvature at the edges is neglected. It can be shown that if the free surface is convex outwards the expression is

$$\pi k \Delta\theta = \frac{2a.b.Q}{r(b^2 - R^2)} - \frac{2R^2Q}{(b^2 - R^2)^{\frac{3}{2}}} \tan^{-1} \frac{a\sqrt{(b^2 - R^2)}}{b\sqrt{(R^2 - a^2)} + R^2} \qquad \text{......(5).}$$

§ 3. APPARATUS

Two sets of apparatus of different dimensions were used, both having a common design shown in figure 2. The liquid film was formed between the surfaces of the cold plate *P* and the heater unit *H*, the latter being supported on *P* by three cylindrical glass pillars each 0·1070 cm. high. Both hot and cold plates were of electrolytic copper, scraped flat and gilded, and were finally tested for flatness against optically flat glass. The plates were 3·460 cm. in diameter in one apparatus and 6·00 cm. in the other. The temperatures of these plates were measured with thermocouples embedded in holes some 2 mm. from each surface and reaching to the centres of the plates.

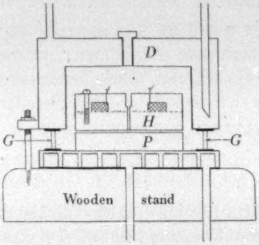


Figure 2.

The cold plate *P* was maintained at a constant temperature by a uniform flow of water through a helical groove cut in the bottom of the plate. The water supply was maintained from a large copper reservoir, both reservoir and leads being heavily insulated.

The heater *H* was a solid copper cylinder in which was embedded a heating-coil of manganin wire of approximately 16Ω resistance. This heater was surrounded by a hollow dome *D* of heavy sheet copper maintained at a uniform temperature by a constant flow of water from a second reservoir. A removable solid copper plug was provided in the top of the dome to replenish the liquid film if necessary during the course of a run.

In order to reduce the evaporation of the film to a minimum it was enclosed in an airtight space by supporting the dome on a glass ring *G* which rested on the cold plate P, the surface of contacts between the glass and metal being sealed with rubber gaskets. The leads to the thermocouples and heating-coil were brought out through these gaskets. In this manner it was possible to saturate the air near the film at the high temperatures, where the evaporation would normally have become unmanageably large, and still keep the film under observation. The film was formed by allowing drops of boiled distilled water to run down a central hole in the heater, bubbles being prevented by lightly packing the hole with lint.

The whole of the apparatus was enclosed in a constant temperature enclosure, consisting of a wooden box lined with thick layers of cotton wool and having glass windows for viewing the film.

§4. MEASUREMENTS OF TEMPERATURES

All temperature-measurements were made with copper-constantan thermoelements, whose e.m.fs. were measured by means of a Wolff potentiometer. Ten microvolts produced a deflection of five divisions on the galvanometer scale, and since it was possible to read this to one tenth of a division, temperatures could be read to better than 0·01° C. The temperature-difference between the dome and the heater was measured by means of a differential couple, while that between the two plates was measured in some cases with a couple used differentially and in others with two separate couples.

The couples were first tested for homogeneity and then calibrated by comparison with a platinum resistance thermometer, whose constants had previously been very carefully determined*, and whose fundamental interval was once again checked to ensure that no change had occurred since its previous calibration. The calculations of temperatures from e.m.fs. were made by Adams' method†.

§5. MEASUREMENT OF POWER

The power supplied to the heating-coil was calculated from the measurement of the potential drop E_1 across the heating-coil and that E_2 across a standard resistance of nominal value 0·1 Ω. The rate of heat-generation was equal to

$$E_1 E_2 / 4{\cdot}18 \times 0{\cdot}09998 \text{ cal./sec.}$$

§6. CORRECTIONS

Effect of curvature of the free surface of the water film. On substituting the dimensions of the apparatus used in equation (5) it was found that a radius of curvature of approximately 2 mm. would produce a change of 1 per cent in the value of k deduced in the less favourable case, that of the smaller apparatus. The film was therefore viewed constantly during a run and the final temperatures were taken when the surface was perpendicular to the plates. At the highest temperatures, where this was sometimes difficult to arrange, the values of k were checked by using equations (3) and (5).

---

* T. H. Laby and E. O. Hercus, *Phil. Trans.* (A), **227**, 63 (1927). We are indebted to Dr Hercus for assistance in calibrating the thermocouples.

† *Amer. Inst. Mining and M. Eng.* p. 165 (1920).

Heat-losses. If conditions are steady so that the thermal capacity of the apparatus does not have to be considered,

$$kA\,\Delta\theta/0\cdot107 = E_1E_2/4\cdot18 \times 0\cdot09998 - L - E,$$

where L is made up of separate heat-losses H_1, H_2, H_3, and H_4.

H_1

H_1 cal./sec. is the heat lost from the heater to the dome per second. As the dome is always kept at a slightly higher temperature than the heater, only conduction has to be considered. The air space was considered as equivalent to that between two concentric cylinders of radii r and b respectively and length $\frac{1}{2}(L+l)$, together with that between two parallel discs of radii r and b and $(L-l)$ apart.

$$H_1 = \pi k_a \Delta t\left(\frac{L+l}{\log_e(b/r)} + \frac{rb}{L-l}\right).$$

k_a* was taken as $5\cdot33 \times 10^{-5}(1 + 0\cdot003\,\theta)$.

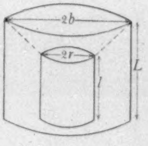


Figure 3.

Δt is the temperature-difference between the heater and the dome and is always negative. For the small apparatus H_1 has values ranging from 0·003 to 0·006, while for the large apparatus, owing to a greater difference $(L-l)$, the values are approximately one tenth as great.

H_2

H_2 cal./sec. is the heat radiated per second from the top to the bottom plate. The emissivity of the gilded surfaces compared with that of a black body was found to be 0·12 and as the maximum value of H_2 attained was 0·0001, H_2 could be neglected.

H_3

H_3 cal./sec. is the heat conducted per second through the glass pillars which have a total cross section 0·0239 cm.² and length 0·1070 cm.

$$H_3 = 3\cdot64 \times 10^{-4}\,\Delta\theta.$$

H_4

H_4 cal./sec. is the heat conducted per second along the leads from the heater to the constant-temperature enclosure.

$$H_4 = 3\cdot14 \times 10^{-5}\,\delta\theta,$$

where $\delta\theta$ is the temperature-difference between the heater and the enclosure. This correction had a maximum value of the order 0·0006 at the highest temperature.

In the case of the larger apparatus a correction was made for any slight change in temperature of the heaters during an experiment.

---

* *International Critical Tables*, **5**.

In order to test the validity of the above corrections and to see whether there was any large heat-loss unaccounted for, a measurement was made of the conductivity of air with each apparatus. $6{\cdot}1 \times 10^{-5}$ was obtained at 0° C., a value somewhat greater than recent values (Trautz and Zündel)[*] which are of the order of $5{\cdot}7 \times 10^{-5}$ but considering the unsuitability of the apparatus for measuring such small conductivities the result must be regarded as satisfactory. A considerable variation is to be found in the literature for the conductivity of air at 0° C., but it seems certain that in these water experiments the amount of heat unaccounted for is less than 1 per cent.

Table 1

θ (° C.)	$\dfrac{E_1E_2}{JR}$	L	E	$\Delta\theta$	$k \times 10^3$	$k \times 10^3$ (calculated)
10·0	·4468	− ·00411	—	3·61	$1{\cdot}42_6$	$1{\cdot}42_6$
13·5	·4421	− ·00357	—	3·55	$1{\cdot}43_4$	$1{\cdot}43_7$
14·4	·5944	− ·00188	—	4·73	$1{\cdot}43_8$	$1{\cdot}44_0$
16·1	·5968	− ·00253	—	4·71	$1{\cdot}45_2$	$1{\cdot}44_6$
17·9	·6013	− ·00246	—	4·72	$1{\cdot}46_0$	$1{\cdot}45_1$
19·8	·5879	− ·00206	—	4·60	$1{\cdot}46_4$	$1{\cdot}45_7$
20·7	·4606	− ·00232	—	3·62	$1{\cdot}45_9$	$1{\cdot}46_0$
20·9	·4524	− ·00349	—	3·55	$1{\cdot}46_6$	$1{\cdot}46_1$
24·5	·5957	− ·00430	—	4·64	$1{\cdot}47_6$	$1{\cdot}47_2$
25·1	·5224	− ·00372	—	4·08	$1{\cdot}47_2$	$1{\cdot}47_4$
25·9	·4236	− ·00141	—	3·27	$1{\cdot}48_4$	$1{\cdot}47_7$
26·6	·5917	− ·00342	—	4·60	$1{\cdot}47_7$	$1{\cdot}47_9$
28·4	·5883	− ·00208	—	4·57	$1{\cdot}47_4$	$1{\cdot}48_5$
29·4	·4687	− ·00328	·0023	3·60	$1{\cdot}48_9$	$1{\cdot}48_8$
29·9	·5857	− ·00256	·0023	4·45	$1{\cdot}50_3$	$1{\cdot}49_0$
30·8	·4647	− ·00314	·0062	3·51	$1{\cdot}50_1$	$1{\cdot}49_3$
34·2	·4720	− ·00302	·0079	3·56	$1{\cdot}49_7$	$1{\cdot}50_3$
36·1	·4808	− ·00180	·0081	3·59	$1{\cdot}50_9$	$1{\cdot}50_6$
39·1	·4647	− ·00322	·0073	3·44	$1{\cdot}52_9$	$1{\cdot}51_9$
42·6	·4744	− ·00093	·0090	3·51	$1{\cdot}51_7$	$1{\cdot}53_0$
47·0	·5776	− ·00610	·0099	4·22	$1{\cdot}55_2$	$1{\cdot}54_5$
47·4	·5842	− ·00179	·0099	4·29	$1{\cdot}53_2$	$1{\cdot}54_6$
50·2	·4275	− ·00137	·0046	3·10	$1{\cdot}56_3$	$1{\cdot}55_5$
54·1	·4315	− ·00280	·0111	3·08	$1{\cdot}56_8$	$1{\cdot}56_7$
60·3	·4315	− ·00348	·0196	2·99	$1{\cdot}58_5$	$1{\cdot}58_7$

Table 2

θ (° C.)	$\dfrac{E_1E_2}{JR}$	L	E	$\Delta\theta$	$k \times 10^3$	$k \times 10^3$ (calculated)
7·4	1·008	·002	—	2·71	$1{\cdot}40_6$	$1{\cdot}41_8$
21·5	1·014	·002	—	2·62	$1{\cdot}46_3$	$1{\cdot}46_3$
34·6	1·271	·003	·0164	3·14	$1{\cdot}51_0$	$1{\cdot}50_5$
49·8	1·007	·006	·0267	2·36	$1{\cdot}56_3$	$1{\cdot}55_5$

Evaporation correction. E cal./sec. represents the rate at which heat is being used in evaporation of the water at the free surface. This was calculated from observation of the rate of change of the curvature of the meniscus and the known latent heat of evaporation at the temperature. Depending as it does on the degree of saturation of the air space the magnitude of this correction varied somewhat irregularly from experiment to experiment.

---

[*] *Z. f. tech. Phys.* **6**, 280 (1931).

§ 7. RESULTS

Tables 1 and 2 show the relevant details of the experiments on water with the small and large apparatus respectively. The authors' results can be best represented by

$$k \times 10^3 = 1{\cdot}39_4\,(1 + 0{\cdot}0023t),$$

the mean departure from this being 0·4 per cent and the maximum departure less than 1 per cent. They are compared with those of previous workers in table 3, where values of k at 0°, 15° and 60° C. and the temperature coefficient α are shown.

Table 3

	$10^5 \times k$ at			α
	0° C.	15° C.	60° C.	
Jacob	132	138	156	·0030
Bridgman	134	139	154	·0022
Martin and Lang	139	144	159	·0023
Kaye and Higgins	145	148	156	·0012

The values of k given by different workers agree better at the higher temperatures. This is difficult to understand, as the most troublesome correction, that due to evaporation, does not enter seriously at the lower temperatures. The chief criticism which can be levelled against the previous work concerns the magnitude of the corrections involved. The evaporation correction in the case of Kaye and Higgins is very uncertain, and the thickness of the water layer, which in no case exceeded 0·5 mm. and fell as low as 0·25 mm., was rather small for the measurement of such relatively high conductivities. The presence of the gallery of liquid in their apparatus would also be expected to give high values of k. The total correction applied to the measured power by Jacob ranges from 2 per cent to 10 per cent. In the present experiments it was only twice above 2 per cent and was usually less than 1 per cent.

§ 8. ACKNOWLEDGMENT

In conclusion we wish to express our indebtedness to Prof. T. H. Laby for his constant interest and the helpful suggestions made during the course of the work.

532.13

THE MEASUREMENT OF THE VISCOSITY OF A MOLTEN METAL BY MEANS OF AN OSCILLATING DISC

BY VAUGHAN H. STOTT, M.Sc.,
The National Physical Laboratory

Communicated by Dr Ezer Griffiths, F.R.S., March 17, 1933. *Read May* 5, 1933

ABSTRACT. Experiments have been made on the viscosity of molten tin by the use of an oscillating disc. The theory of the method has been investigated, and it has been found necessary to calibrate the apparatus on molten metals having viscosities and densities not too different from those of the metals which are to be investigated. In the case of tin, the values of the viscosity at different temperatures have been determined by Sauerwald and Töpler by the capillary-tube method, and the present experiments have lengthened the range of temperature for which the viscosity of tin may be regarded as fairly well established. Discontinuity in the (viscosity, temperature) curve of molten tin at temperatures near its freezing point must be regarded as very improbable, and certainly does not occur at temperatures more than 6° C. above that point.

It has been shown that the method of the oscillating disc may be used in cases where other methods of measurement are inapplicable, but it is desirable to verify the measurements which have been made by Sauerwald and his co-workers by the capillary-tube method in order that full reliance may be placed on the values of the viscosities of the metals which are most suitable for the calibration of the oscillating-disc type of apparatus.

§ 1. GENERAL CONSIDERATIONS

PUBLISHED measurements of the viscosities of molten metals are scanty, and, for the most part, unconfirmed. Moreover, the reliable measurements have all been obtained by determining the pressure-difference required to drive a measured quantity of liquid per second through a capillary tube of known effective resistance. The viscosities which have been measured are all very small, the kinematic viscosities being usually considerably less than that of water, and in no case exceeding it. (The kinematic viscosity $\nu = \eta/\rho$, where η is the viscosity, and ρ the density.) There are but two other established methods of measurement which offer any hope of success in place of the capillary-tube method. These are the Couette or Margules method, and the logarithmic-decrement method. In the former it is necessary to determine the torque which must exist between two concentric cylinders, rotating at different velocities, when the annular space between the cylinders is filled with the liquid under investigation. For liquids of low kinematic viscosity, this method is difficult for a variety of reasons, and even in the case of water Couette was unable to dismantle his apparatus and reassemble it without producing a very considerable change in its constants. The added difficulties attendant on the use of high temperatures seem to rule out the use of this type of apparatus. ν, η, ρ

The logarithmic-decrement method is experimentally the simplest of all, the main difficulties being of a theoretical nature. As usually employed, it consists in the determination of the logarithmic decrements between successive maximum displacements of a solid of revolution which is immersed in the liquid, and executes, about its vertical axis of symmetry, rotational oscillations under the control of a torsion wire, or a bifilar suspension.

The theory of such an instrument is in its simplest form when the amplitudes of vibration are very small and the vessel containing the liquid is very large compared with the dimensions of the oscillating body. In the case of molten metals the inertia of the liquid is great compared with its viscosity, and the movements of the liquid contained in a very large vessel are inappreciable at comparatively small distances from the surface of the oscillating body. The variations in the rate of decay of the oscillations of the latter are, therefore, not seriously affected by small changes in the dimensions of the containing vessel or in the height of the liquid contained therein, nor is it necessary that the oscillating body should be very accurately placed in its proper position within the vessel. Those who are familiar with the peculiar difficulties of high-temperature work will realize the very great importance of these considerations with regard to the choice of a suitable method of measurement. In comparison with the capillary-tube method, the logarithmic-decrement method has also the advantage of permitting a considerable choice in the materials from which the oscillating body and the containing vessel are formed. Capillary tubes, on the other hand, can only be made of silica, or glass for very low temperatures, and if the containing vessel be friable, care must be exercised to prevent any particles of dust from entering the capillary tube. As silica is attacked by aluminium and certain other metals, the capillary-tube method is inapplicable to them. Owing to devitrification, silica tubes cannot be used at temperatures greatly in excess of 1100° C. Unfortunately, the logarithmic-decrement method has several disadvantages. In the first place, the theory underlying the measurements is very complex, and can be applied to absolute measurements only in circumstances which are experimentally inconvenient. Secondly, the actual design of an oscillating system is a matter of some delicacy, a compromise being necessary between a considerable number of conflicting requirements. To a smaller extent this remark applies also to the capillary-tube method.

§ 2. APPARATUS

As the work of Fawsitt* had demonstrated the practicability of the logarithmic-decrement method, it was decided to give this a trial. As an oscillating body a disc of alumina, somewhat thicker at the centre than at the periphery, was chosen. The slight taper in the section facilitates the escape of air bubbles which might adhere to the under surface of the disc if this surface were horizontal. The tapered disc is less liable to warp during drying and firing than one with parallel surfaces, and the extra thickness in the centre does not add very much to the volume. This is important, for it is desirable to use a body of such a shape that its volume is as small as possible for a given degree of damping of its oscillations. This is because the buoyancy of the disc on immersion in the molten metal reduces the tension of the suspension wire, and raises the effective centre of gravity of the suspended system to an extent proportional to the density of the liquid in which it is immersed.

---

* *Proc. R. S.* A, **80**, 290 (1908).

Although pure alumina was finally selected as a material for both the disc and the containing vessel, graphite was used in the early experiments, as the ease with which it could be machined rendered its use attractive. Unfortunately, it was found to disintegrate to a slight extent, and measurements in mercury were vitiated by the formation of a scum on the surface.

The suspended system finally adopted included the alumina disc, which had a diameter of 1·8 in., with a short stem of diameter $\frac{3}{16}$ in. fixed in a steel disc, $\frac{1}{4}$ in. thick and 3 in. in diameter, which acted as a sinker and as a mass of suitable moment of inertia. To the top of the steel disc was attached a steel rod, $\frac{3}{16}$ in. in diameter, extending upwards to the cold part of the furnace in which the experiments were conducted. The top of this rod was fixed to the lower end of the torsion wire, which was of phosphor bronze, 0·006 in. in diameter, and rather less than a foot in length. The two discs are shown in figure 1. The period of a complete oscillation of the system was always very close to 28 sec. The upper end of the steel rod carried, in the earlier experiments, a light mirror, and later a light aluminium disc, 3 in. in diameter, having a rim bearing a scale divided into 500 parts extending all round the circumference.

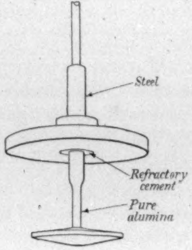


Figure 1. Construction of disc.

The whole of this system, together with a pot of metal, could be enclosed in a wire-wound electric furnace in which an atmosphere of hydrogen was maintained. The furnace proper had an internal diameter of $3\frac{1}{4}$ in. and a length of 2 ft. The furnace tube, of silica, extended some 6 in. above the top of the furnace proper, this extension being water-cooled. A brass tube closed at its upper end was sealed to the top of the silica furnace tube, and formed a further extension in order to carry the torsion head. A window of optical glass was sealed into the brass tube at the level of the mirror, or the circular scale, thus permitting measurements to be made of the amplitudes of the oscillations with the aid of a telescope, a distant scale being used for the early experiments using the mirror, while direct readings of the divided scale were made during the later experiments.

Oscillations could be started and controlled by the rotation of the torsion head; as hydrogen was used in the apparatus, this entailed a gas-tight joint. The torsion wire was soldered at its upper end into a bronze rod $\frac{1}{4}$ in. in diameter, which was accurately fitted to a bronze sleeve some 5 in. long through which it passed. The rod was lubricated with vaseline, and a small cup was turned out of the top of the sleeve to act as a reservoir for lubricant. Such a joint, if well made, will hold a vacuum for a fortnight without the lubricant having to be replenished. It has the advantage of permitting vertical movements of the centre rod in addition to movements of rotation. The disc could therefore be lowered into the molten metal at the start of a series of measurements and raised from the metal at the end of the experiment. A simple arrangement enabled the rod to be clamped at the correct height when required, so that oscillations could be initiated by means of a rotary motion without disturbing the vertical adjustment.

The pot of metal was placed in the middle of the furnace on an inverted, closed hollow cylinder of refractory material filled with asbestos wool. This cylinder, occupying almost the whole width of the furnace tube, acted as an effective heat-insulator. A platinum-rhodio-platinum thermocouple, enclosed in a silica sheath, was inserted into the furnace from below through suitable apertures, a gas-tight joint being made at the bottom of the furnace. The top of the thermocouple sheath touched the bottom of the pot of metal. A similar heat-insulating cylinder, with a central tube of bore $\frac{1}{2}$ in. through which passed the rod carrying the discs, was suspended from the upper end of the furnace tube. The furnace winding was uniformly spaced, and therefore the variations of temperature in different parts of the free space, some 7 in. long in the middle of the furnace, were negligibly small. The current through the furnace was thermostatically controlled, and no appreciable changes of temperature occurred during a measurement of the logarithmic decrement.

§ 3. THEORY OF THE EXPERIMENTAL SYSTEM

We shall now consider the theory of these experiments when the maximum velocity of the disc is very small. In this case it is found by experiment that the logarithmic decrement of the amplitude of vibration is independent of the value of the amplitude.

The simplest equation of motion which yields this result may be written

$$K\frac{d^2\theta}{dt^2} + \lambda\frac{d\theta}{dt} + n^2\theta = 0 \qquad \text{......(1)},$$

t

where θ is the angular displacement of the disc, and K, λ, and n are constant during a series of oscillations.

θ, K, λ, n

If Λ be the logarithmic decrement of a system conforming with this equation,

Λ

$$\Lambda = \lambda T/2K,$$

where T is the time of vibration of the system.

T

Now equation (1) is known to apply to the case of an ellipsoid of revolution oscillating with a small amplitude about its generating axis in a fluid contained in a vessel which has also the shape of an ellipsoid of revolution having its generating axis coincident with that of the oscillating body. It is therefore reasonable to assume that an equation of the form (1), with suitable values of K and λ, is applicable to the case of the disc and vessel used in the present experiments.

We may observe that n is a property of the suspension wire and λ a property of
I_0 the liquid, while K may be regarded as the sum of I_0 and I_1, where I_0 is the moment
I_1 of inertia of the suspended system and I_1 represents additional inertia due to the motion of the liquid. Now inasmuch as λ depends upon the liquid, it must depend upon the viscosity η, and the density ρ. It must also depend on the scale of the
L apparatus, which may be represented by a length L, and on the time of vibration T.

We may write, then,

f

$$\lambda = f(\eta, \rho, L, T).$$

Now $\lambda/\eta L^3$ is dimensionless,

ϕ

$$\therefore \frac{\lambda}{\eta L^3} = \phi\left(\frac{\eta T}{\rho L^2}\right),$$

the function on the right including all possible dimensionless combinations which can be formed from η, ρ, L, and T.

Now
$$\Lambda = \lambda T/2K,$$
$$\therefore \frac{2K\Lambda}{\eta T L^3} = \phi\left(\frac{\eta T}{\rho L^2}\right).$$

But
$$\frac{K}{I_0} = \frac{T^2}{T_0^2(1 + \Lambda^2/4\pi^2)},$$

T_0 where T_0 is the time of vibration of the system when undamped or, to a sufficient approximation, when oscillating in air. I_0, being the moment of inertia of the suspended system, is independent of the particular liquid.

Hence $\Lambda T/\eta\,(1 + \Lambda^2/4\pi^2)$ is the same function of $\eta T/\rho$ for all liquids, provided that the dimensions of the apparatus remain unchanged.

Now, in Fawsitt's experiments, K/I_0 and T/T_0 were practically unity in every case, so that if the amplitudes of vibration were small enough we should expect to find that Λ/η is a function of η/ρ, or, of course, that η/Λ is a function of η/ρ.

Figure 2 shows η/Λ plotted against η/ρ from the data obtained by Fawsitt in calibration. It will be seen that all the points are very close to a single curve; the deviations, regarded as equivalent to errors in the logarithmic decrements, being slightly less than the corresponding errors which occur when the relation used by Fawsitt is assumed to be true, namely,

$$\Lambda_{10} = C_1\sqrt{(\eta\rho)} + C_2\eta + C_3\,\eta\rho,$$

Λ_{10} where Λ_{10} is the logarithmic decrement calculated to the base 10. It is assumed throughout that Λ has always been corrected by subtracting from the observed value the decrement found when the suspended system swings, without the lower disc, in air or hydrogen as the case may be, at the temperature of the main experiment.

In the present experiments, the first measurements were made with very small amplitudes, the greatest being some 7°. It was found, however, that the viscous forces were so small at these low amplitudes that the experimental errors were somewhat serious. No change of logarithmic decrement with amplitude was actually observed under these conditions, although in the case of mercury, turbulence is liable to occur at an amplitude of about $3\frac{1}{2}°$ when a disc having the same dimensions and period as that used is caused to oscillate in a very large quantity of fluid*. At first sight, then, experiments carried out with larger amplitudes would be expected to lead to a logarithmic decrement varying with amplitude, and to the possible failure of the simple method of calibration already obtained. It was, however, noticed that Fawsitt's discs were little smaller than those used in the present experiments and that his times of vibration were considerably shorter. Moreover, the amplitudes used by Fawsitt must have been large, for they were measured by means of a pointer moving over a scale divided into degrees, whereas in the present case the maximum amplitude was only about 7°, this being divided on the scale into 500 parts. It appeared probable, then, that Fawsitt also exceeded the theoretical limits of the simple theory, and that it might be found even in the case of the higher amplitudes that we may have

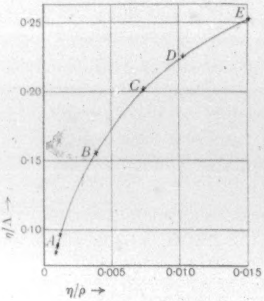


Figure 2. *A* mercury. *B* chloroform. *C* benzene. *D* water. *E* ethyl alcohol.

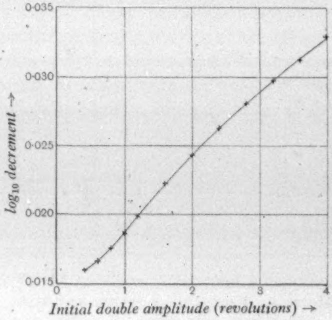


Figure 3.

$$\frac{\Lambda T}{\eta\,(1+\Lambda^2/4\pi^2)} = \psi\left(\frac{\eta T}{\rho}\right)$$

or, sufficiently closely in our case,

$$\frac{\Lambda T}{\eta} = \psi\left(\frac{\eta T}{\rho}\right).$$

It was anticipated, however, that the logarithmic decrement would be a function of amplitude, and that the former would have to be calculated for a particular initial value of the latter.

Accordingly, the apparatus was modified in the manner already described, and measurements were made on mercury, chloroform, benzene, water, and isopropyl alcohol. It was found that the results depended upon the orientation of the torsion head. The effect was traced to the fact that the torsion wire was not soldered quite vertically into the centre of the disc on which the angular displacements were read. In consequence, this disc was not rotating exactly about its centre. By repeating the measurements with the torsion head rotated through 180°, and taking the mean of the two sets of measurements, this error could be eliminated.

---

* A. Foch and J. Bariol, *Comptes Rendus*, **193**, no. 19 (1931).

Figure 3 shows a typical curve for water, the logarithmic decrement being plotted against the double initial amplitude; that is, against the angle between the maximum displacement to the left and the succeeding maximum displacement to the right. Subsequent calculations were based upon logarithmic decrements associated with an initial double amplitude of 1½ revolutions, but the general nature of the results is unchanged if one, or two revolutions, be taken as fiducial values. For practical reasons it was not convenient to work with values outside these limits, the highest precision being obtained from results based upon an initial double amplitude of 1½ revolutions, which was therefore used as the fiducial amplitude.

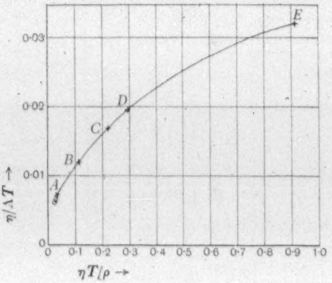


Figure 4. *A* mercury, $\rho=13{\cdot}55$, $\eta=0{\cdot}0156$. *B* chloroform, $\rho=1{\cdot}492$, $\eta=0{\cdot}00614$. *C* benzene, $\rho=0{\cdot}8845$, $\eta=0{\cdot}00706$. *D* water, $\rho=0{\cdot}999$, $\eta=0{\cdot}01054$. *E* isopropyl alcohol, $\rho=0{\cdot}809$, $\eta=0{\cdot}0264$.

The results first obtained for various liquids are shown in figure 4, but the lowest two points, which represent the behaviour of mercury at comparatively high temperatures, were obtained at a later stage. It will be observed that the points which were first obtained lie very close to a smooth curve.

During the course of these measurements special experiments were performed in order to ensure that no errors were liable to occur as a result of inaccurate centring of the pot, incorrect quantity of liquid, incorrect height of the disc, or inclination of the torsion head from the vertical. It was found that very little care was sufficient to reduce the errors due to any of these causes to a value much lower than that of the errors found on repeating the measurements under similar conditions. The containing vessel used had an internal diameter of 2·6 in. and was filled with liquid to a height of 1½ in. before the immersion of the disc. The clearance between the circumference of the disc and the cylindrical surface of the pot was, therefore, 0·4 in. The middle of the disc was 0·84 in. above the bottom of the liquid.

The values of the viscosities and densities of the liquids used were obtained from the *International Critical Tables* for the particular temperatures of the experiments, except in the cases of chloroform and isopropyl alcohol. The values for these two liquids were measured in the laboratory in the usual way.

§4. CORRECTIONS NECESSARY AT HIGH TEMPERATURES

As the calibration curve of figure 4 appeared to be satisfactory, a series of concordant measurements was made on molten tin in an atmosphere of hydrogen. Certain corrections had to be made owing to the high temperatures at which the experiments were performed. In connexion with the corrections we shall consider again the theory of dimensions, but we shall not assume the logarithmic decrement to be independent of the amplitude. We shall assume merely that Λ depends upon η, T, ρ, L, I_0, and θ, where L is a linear magnitude representing the size of the apparatus, I_0 is the moment of inertia of the suspended system as before, and θ is the initial amplitude, the logarithmic decrement Λ being calculated from the values of two successive double amplitudes. A knowledge of the position of equilibrium of the oscillating system is not required in this case.

Since Λ is dimensionless,

$$\Lambda = f\left(\frac{\eta T}{\rho L^2}, \ \frac{\rho L^5}{I_0}, \ \theta\right) \qquad \ldots\ldots(2),$$

the expression on the right including all possible dimensionless quantities depending upon η, T, ρ, L, I_0, and θ.

It will be observed that when T, L, I_0, and θ are constant, Λ becomes a function of η/ρ and ρ, that is, an unknown function of two variables, whereas when the amplitudes are very small Λ/η is a function of η/ρ, that is, of one variable; and since η is known for every calibrating-liquid, Λ is immediately calculable when the value of Λ/η is known.

Returning to the question of corrections, we may now point out that the results of the calibration may be written approximately

$$\Lambda \propto \sqrt{(\eta T \rho)} \qquad \ldots\ldots(3).$$

For all the liquids used, the constant of proportionality fell within the range between 0·032 and 0·038.

Comparing equations (3) and (2), we obtain

$$\Lambda \propto \frac{L^4}{I_0}\sqrt{(\eta T \rho)} \qquad \ldots\ldots(4).$$

Three independent thermal expansions are to be considered in connexion with experiments at high temperatures, namely that of the liquid, those of the alumina disc and the containing vessel, and that of the steel inertia disc. The preliminary experiments showed that the effect of the expansion of the liquid may be ignored. The same is true of the lowering of the disc with respect to the pot, which occurs at high temperatures owing to the difference in the rates of expansion of steel and silica. The effects of the expansions of the two discs must, however, be allowed for in accordance with equation (4)*.

Since most of the inertia of the system is due to the steel disc, a knowledge of the coefficient of expansion of steel is sufficient for the calculation of the change of I_0. This value can also be obtained by comparing the times of vibration of the apparatus in an atmosphere of hydrogen at high and at low temperatures, for, owing to the water cooling, the elasticity of the suspension wire is substantially constant.

These corrections are actually very small, since the effects of the expansions of the alumina and steel discs have opposite effects on the value of Λ, resulting in a zero correction at the melting point of tin and a correction of slightly less than 1 per cent of Λ, or rather less than 2 per cent of η, at 800° C. At still higher temperatures the correction grows rapidly. The principles involved have been explained in some detail because experiments might be made by other workers at considerably higher temperatures, and the explanation given by Fawsitt appears to be incorrect. It may be mentioned in passing that the expansion of all forms of calcined alumina is substantially the same as that of fused alumina so long as the heating, in the former case, is insufficient to produce a permanent contraction†. The discs used in our experiments were made of pure alumina by the process of slip casting and were fired to 1530° C. The stems were made separately, the ends being turned in the lathe. The lower end of the stem made a tight tapered fit in the disc, and the upper end was fixed in the steel disc with the aid of a refractory cement, the operation being conducted with great care in the lathe.

As was previously mentioned, the logarithmic decrements require correction for the influence of the resistance of the gas in the apparatus, and the imperfect elasticity of the suspension wire. This correction depends very considerably on temperature; the logarithmic decrement of the system in hydrogen, without the alumina disc, varies from 0·002 at 16° C. to 0·0035 at 800° C. The change of this quantity with temperature was not considered by Fawsitt. In the present experiments this correction amounts, in the case of tin at a temperature of 800° C., to 7 per cent of the logarithmic decrement or 14 per cent of the apparent value of the viscosity.

§ 5. RESULTS OF MEASUREMENTS ON TIN, AND COMPARISON WITH THOSE OF OTHER INVESTIGATORS

The logarithmic decrements in the case of tin for a fiducial double-amplitude of $1\frac{1}{2}$ revolutions are shown in figure 5. On calculation of the viscosity values with the aid of figure 4 and with values of ρ obtained from the *International Critical Tables*, it was found that the temperature coefficient of viscosity was much less than that found by Sauerwald and Töpler*, the two curves which express the relation of viscosity to temperature crossing at about the middle of the range. A careful consideration of the work of Sauerwald and Töpler, who used the capillary-tube method, failed to disclose any probable source of serious error, the accuracy of the experiments being estimated by these authors as within about 1 per cent.

---

* The expansion of the pot has no appreciable effect on the value of Λ, the effect of a change of L being really ascribable to the change in dimensions of the alumina disc alone. This remark applies only to the conditions of our experiments. For example, if we were dealing with liquids of extremely high viscosity we should find Λ proportional to $L^3 \eta T / I_0$, and in this case the effect of a change of L would not be ascribable to the change in dimensions of the disc alone, but would include the effect of the expansion of the pot and the liquid. As the liquid would expand at a different rate from that of the disc and pot in such a case, special experiments would be needed to determine the correction.

† George E. Merritt, *Trans. Amer. Electrochem. Soc.* **50**, 165 (1926); H. Forestier, *Annales de Chimie*, **9**, 316 (1928).

A consideration of the viscosities and densities of the liquids used in calibration, suggested that the proximity of the various points to the calibration curve of figure 4 might be fortuitous, and that divergences might be found in the case of other liquids since, as had been explained, there is no strong reason for the belief that the representative points should lie on a single curve in the case of oscillations of large amplitude. In order to test this supposition, liquids of high density with various viscosities are required. The practical choice is restricted to mercury at high temperatures if we leave out of account other metals, such as tin and lead, the viscosities of which cannot be regarded as established with a high decree of certainty. Experiments were therefore carried out on mercury, beginning at room temperatures. Difficulty in making consistent measurements was initially experienced owing to slight contamination of the disc with the tin previously used. Less than one part in a million of impurity in mercury results in the production of a surface layer of remarkable mechanical strength, which seriously interferes with the measurements. It was mainly owing to the disturbing influence of surface effects in the case of mercury that the earlier experiments at very small amplitudes had to be abandoned. Fawsitt, who melted his tin in air, had to cover the surface with a flux. If we assume the correctness of Sauerwald's values, Fawsitt obtained a value some 30 per cent too high for the viscosity of tin at a low temperature. He recognized, however, the probability of a considerable error of this nature. In the present experiments it was found that the very small amount of contamination of the disc could be removed by repeated washing with pure mercury, after which the original calibration was repeated closely several times. These experiments were carried out in air, both inside and outside the furnace, proper correction being made in each case for the part of

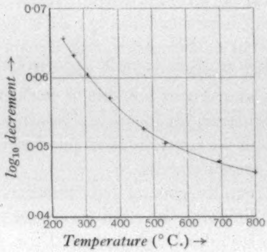


Figure 5. Results for tin.

---

* F. Sauerwald and K. Töpler, *Z. f. Anorganische und Allgemeine Chemie*, **157**, 117 (1926).

the decrement due to subsidiary resistances. On raising the temperature of the mercury it was found that surface contamination occurred, and finally, as a result of an accident, the disc was broken. A new disc gave concordant results at room temperatures, the decrement being about 10 per cent higher than those measured with the old disc. It was assumed that this ratio is independent of viscosity, and concordant measurements were then made at higher temperatures in an atmosphere of hydrogen, which suppressed the contamination of the surface.

The results obtained are represented in figure 4 by the lowest two points, and, as was to be anticipated, they do not lie strictly on the original calibration curve.

It was also found that an equation of the kind used by Fawsitt gave results similar to those calculated from the calibration curve, and therefore inconsistent with Sauerwald's values for tin. Agreement may be obtained by the use of an equation of the form

$$\Lambda = A\sqrt{(\eta T\rho)} + B\eta T\rho + C\eta T + D\rho,$$

but even in this case the best values of the constants cannot be determined sufficiently accurately without the use of some metal having a lower density than that of mercury. It follows that this method of measurement must always be based upon calibration performed on metals having hydrodynamical properties fairly close to those of the metal under investigation, unless it be possible to work at very low amplitudes. At very high temperatures, however, the logarithmic-decrement method appears to be the only practicable one, and the considerations put forward may be of assistance to anyone undertaking such measurements.

Although, as we have seen, the general determination of Λ as a function of η, T, and ρ, is a matter of great difficulty, the relations appear to be simpler if we restrict our enquiries to the case of liquids of high density. Thus, the results of the measurements on tin and mercury may be expressed by the simple relation

$$\Lambda = 0{\cdot}0101 + 0{\cdot}0278\sqrt{(\eta T\rho)},$$

the greatest deviation being less than 1 per cent of the value of Λ*. It is interesting to note that Thielmann and Wimmer† calibrated a somewhat similar apparatus, using for the purpose mercury, tin, and bismuth, and assumed that

$$\Lambda = x_1(\eta\rho)^{\frac{1}{2}} + x_2\eta\rho + x_3(\eta\rho)^{\frac{3}{2}},$$

where x_1, x_2, and x_3 are constants. Details are not available, however, of the values of these constants, nor of the amplitudes and times of vibration employed. Great difficulties were met by these authors in connexion with oxidation at the surface of the metal, and it is probable that the present experiments on tin are the first in which this difficulty has been overcome at high temperatures. These experiments have also permitted an extension of Sauerwald's data on tin. Figure 6 shows the values of Λ, plotted against the values of $\eta^{\frac{1}{2}}$ obtained from Sauerwald's smoothed results. By extrapolating this curve for a short distance at each end we may calculate values of η, with the aid of our measurements of Λ, for temperatures some 60° lower and 50° higher than the range covered by Sauerwald. From these calculations, and Sauerwald's smoothed values, the following table has been constructed.

---

* The formula is, of course, based on Sauerwald's values for the viscosity of tin between 300° C. and 750° C.

† *Stahl und Eisen*, **47**, 389 (1927).

Temperature (° C.)	η (poises)	Temperature (° C.)	η (poises)	Temperature (° C.)	η (poises)
240	0·0191	420	0·0133	620	0·01025
260	0·0182	440	0·0129	640	0·01005
280	0·0174	460	0·0125	660	0·00985
300	0·0167	480	0·0122	680	0·00965
320	0·0160	500	0·0118	700	0·00945
340	0·0154	520	0·0115	720	0·0093
360	0·0148	540	0·01125	740	0·00915
380	0·0143	560	0·0110	760	0·0090
400	0·0138	580	0·0107	780	0·00885
—	—	600	0·0105	800	0·0087

No discontinuity of viscosity as a function of temperature was observed down to a temperature of 238° C., six degrees above the solidification point. Fawsitt approached this point so closely that partial solidification of the melt actually occurred, but no discontinuity was observed. We may therefore assume continuity down to the freezing point of the tin. The viscosity at this temperature (232° C.) is 0·0195 poise.

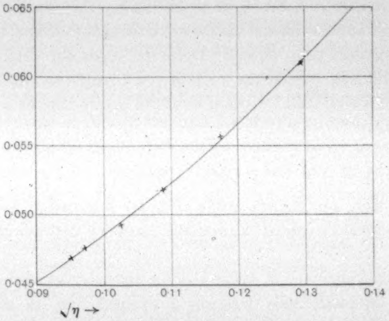


Figure 6. Results for tin.

It has been assumed that the experiments of Sauerwald and Töpler are substantially correct, this assumption being based upon a critical study of their method. Measurements have also been made by Plüss* by a similar method, but with rather less refinement. At a temperature of 280° C. Plüss found a value for η about 3 per cent lower than that subsequently found by Sauerwald and Töpler. At a temperature of 390° C. the discrepancy amounts to rather more than 6 per cent, the variation of viscosity with temperature found by Sauerwald and Töpler being definitely less than that found by Plüss. No other reliable measurements appear to have been made.

---

* *Z. f. anorganische und allgemeine Chemie*, **93**, 1 (1915).

The most recent measurements of the fluidities of a large number of molten metals and alloys have been made by Losana*. The values are said to be relative to the fluidity of tin at a temperature of 300° C. They were determined for the most part with the aid of an oscillating cylinder, no precautions being taken against oxidation other than covering the crucible with a sheet of asbestos. The method of calculating even relative values is erroneous, and a comparison of the results for mercury and tin reveals serious inconsistency if Sauerwald's values are approximately correct. Since, however, the effect of oxidation enters into foundry practice, Losana's results correspond in some degree with that practice, to the limited extent to which considerations of fluidity have a determining influence in connexion with the ease of production of castings.

§ 6. CONCLUSION

The general conclusion emerges, from the present work, that the oscillating-disc method of measuring the viscosities of molten metals is capable of yielding satisfactory results if proper attention be given to the theoretical principles involved, and if the calibration be based on metals having densities and viscosities of known values, which should not be very different from those of the metals under investigation. For this purpose it is desirable to check, by the capillary-tube method, the values obtained by Sauerwald and his co-workers, and perhaps, to extend them. The oscillating-disc method may then be used for cases to which the capillary-tube method is inapplicable, but in the case of the former method it is essential that thorough precautions should be taken to avoid errors due to contamination of the surface of the melt.

DISCUSSION

Mr J. H. Awbery. The figures in the table are interesting, even though I believe they are only Sauerwald's values extrapolated, and not deductions from the author's experiments.

If $\log \eta$ is plotted against $1/\theta$, where η is the viscosity and θ the absolute temperature, the points lie moderately well on a straight line, in accordance with the formula given recently by Andrade. It has been suggested by R. O. Herzog and H. C. Kudar† that the slope b of the line is connected with the latent heat of fusion of the substance concerned. According to their theory, the latent heat of tin comes out at 12·1 gm.-cal./gm., which may be compared with the calorimetrically determined value of 14·6‡ found by Dr Griffiths and the speaker.

I have said that the author's table only consists of Sauerwald's values extrapolated. The method is a little more subtle than if he had merely plotted η against θ and extrapolated the curve with a spline. Suppose he had adopted the following alternative method: Draw, as curve A, any one-valued continuous function of θ, which need not be defined by any analytic expression whatever, but is to be defined

[*] Luigi Losana, *Il Notizario Chimico-Industriale*, **2**, 1, 63, 121 (1927).

[†] *Z. f. Phys.* **80**, 217 (1933).

[‡] *Proc. Phys. Soc.* **38**, 378 (1926).

for a range of values of θ greater at each end than the range of values covered by Sauerwald's experiments. As curve B, plot Sauerwald's values of η against this function $f(\theta)$. Curve B will only exist over the range covered by Sauerwald. Now by extending curve B we can draw up a table of values of η against $f(\theta)$ over a wider range, and this is an extrapolation of Sauerwald's values only. Once this is done, the table is converted easily to a table of η against θ, by the aid of curve A. The extrapolation makes no use of the properties of the function f, except that the latter is taken to be continuous.

This method is the one adopted by the author, who takes $f(\theta)$ as equal to Λ, the experimental logarithmic decrement, for which experiment alone can and does answer the question as to continuity.

Is it too late to ask him to give his experimental results? If Sauerwald's work should be repeated and not confirmed, the necessary modifications in the author's table could not be made without this information. Moreover, if it should ever prove possible to provide a calibration curve, of the nature of figure 4, applicable to the conditions of these experiments, the original data would be of great value.

Mr A. J. Lewis. In searching for a method to extend the knowledge of the viscosity of tin, I decided against the logarithmic-decrement method for various reasons: (*a*) the effects of slight contamination of the surface by oxide and other impurities seem to be almost as great as in the capillary method, and the exposed area is greater. In particular, imperfections near the suspension seem to have an abnormal effect; (*b*) because results depend on the elastic properties of a suspension at different temperatures; (*c*) because the theory is in a highly complicated and rather uncertain state. The method cannot be used for absolute determinations, and relative measurements cannot be made with such certainty as by the capillary method. I have therefore adopted the capillary method and am at present engaged in measuring the viscosity of tin by it. These objections have been met in a masterly way by the author of the present paper. In connexion with (*a*) I would like to ask if greater difficulty was experienced in overcoming oxidation troubles at temperatures near the freezing point than at higher temperatures. Sauerwald and Töpler were unable to obtain satisfactory results below 300° C. on account of this increased difficulty.

Author's reply. In reply to Mr Awbery: I am very interested to hear that there may be a connexion between viscosity, temperature, and latent heat. The question raised with regard to the extension of Sauerwald's values is even more subtle than Mr Awbery suggests. His explanation of my procedure, whilst mathematically correct, is physically incomplete. The logarithmic decrement Λ is essentially a function of the viscosity η and is only incidentally a function of temperature. (The density ρ and the time of vibration T have each an influence on Λ but their variations were very small, and both ρ and T were continuous functions of η. This is obvious in the case of ρ. The explanation in the case of T follows from the fact that the variations of T were due to the variations in the dimensions of the discs as a result of temperature changes, and it turns out that the viscosity of tin is a continuous function of temperature.) The relation between Λ and η was established by determining Λ at a number of different temperatures, and obtaining the corresponding values of η from Sauerwald's work. The next step was to extrapolate the curve connecting Λ with $\sqrt{\eta}$. The relationship between these quantities has a hydrodynamic basis which, except for the small effects due to variations of ρ and T, is independent of the (viscosity, temperature) curve of tin. Furthermore, it is reasonable to suppose that the former curve is continuous, for the effects of discontinuities due to the turbulent flow in the liquid are smoothed because each oscillation of the system involves a range of velocities from zero to a maximum value. For the same reason the (logarithmic-decrement, amplitude) curve is continuous, as may be seen from figure 3. Finally, it may be noted that the procedure which I adopted would probably have given correct results even had there been a discontinuity in the (viscosity, temperature) curve of tin in the neighbourhood of the melting point. It is evident, therefore, that the method involves more than the mere extrapolation of Sauerwald's curve. Considerations of space hardly justify the publication of all the experimental results, which would probably be considerably modified by comparatively small changes in the experimental arrangements.

In reply to Mr Lewis I may say that no difficulties were encountered in connexion with the measurements on tin at any temperature. Indeed, these measurements were more concordant than those made for the purpose of calibration. I am very glad that Mr Lewis is checking Sauerwald's results, as circumstances prevent my undertaking similar work.

621.317.332

TWO SIMPLE METHODS OF ABSOLUTE MEASUREMENT OF ELECTRICAL RESISTANCE IN TERMS OF INDUCTANCE AND FREQUENCY

By H. R. NETTLETON, D.Sc., Lecturer in Physics, Birkbeck College

AND

E. G. BALLS, M.C., B.Sc., A.I.C., Birkbeck College

Received January 25, 1933, *and in revised form March* 4, 1933.
Read May 5, 1933

ABSTRACT. In the first method a sinusoidal alternating current of some 15 mA. derived from a valve oscillator and of frequency equal to that of a König tuning-fork is allowed to induce an equal current in a secondary circuit. The equality of amplitude of the primary and secondary currents is judged with the aid of a Westinghouse instrument rectifier. The resistance of the secondary circuit is given by the expression

$$S = 2\pi n \sqrt{(M^2 - N^2)},$$

where n is the frequency, N the self-inductance of the secondary and M the mutual inductance between the primary and secondary. With standard forks of frequencies 256, 320, 384 and 512, resistances have been measured ranging from 16 Ω to 67 Ω.

In the second method equal primary and secondary currents of known frequency are also produced and are further adjusted to be in quadrature. A simple arrangement is thereby derived which enables Campbell's two-phase alternating-current method of measuring resistance to be carried out in the laboratory.

In both methods a visibly beating circuit is employed which enables the frequency of the current used to be tuned easily, with precision, to that of a valve-maintained fork. This beating circuit is also of value in checking the relative accuracy of forks whose frequencies are very approximately in simple ratio to one another.

---

§ 1. PRINCIPLE OF THE FIRST METHOD

A PRIMARY circuit consists of a valve oscillator, resistance R, relatively large inductance L and neutralizing capacitance K. A secondary circuit of small self-inductance N and having a mutual inductance M, greater than N, with the primary circuit, has a total resistance S. The amplitudes of the primary and secondary currents are adjusted to equality by varying S or M, while the frequency n of the currents is adjusted to that of a valve-maintained König tuning-fork so that the beats, rendered visible, are of the order of 1 a minute. R L, K N, M S n

Under such conditions the resistance of the secondary circuit is given by the relationship

$$S = 2\pi n \sqrt{(M^2 - N^2)} \qquad \ldots\ldots(1).$$

This expression readily follows* from the well-known equations of a primary and secondary circuit, namely

$$\left(L - \frac{1}{\kappa\omega^2}\right)\frac{di_1}{dt} + M\frac{di_2}{dt} + Ri_1 = Ee^{j\omega t} \qquad \ldots\ldots(2a),$$

$$M\frac{di_1}{dt} + N\frac{di_2}{dt} + Si_2 = 0 \qquad \ldots\ldots(2b),$$

i_1, i_2 where i_1, i_2 are the respective instantaneous values of the primary and secondary
ω currents when a sinusoidal alternating e.m.f. of pulsatance ω equal to $2\pi n$ is applied
to the primary circuit. For these equations give, for the ratio of the currents,

$$i_2/i_1 = -Mj\omega/(S + Nj\omega) \qquad \ldots\ldots(3).$$

Thus the ratio of the secondary and primary current-amplitudes is in general $M\omega/\sqrt{(S^2 + N^2\omega^2)}$, and equation (1) results when these amplitudes are equal.

§ 2. THE EXPERIMENTAL ARRANGEMENT FOR METHOD 1

The primary circuit. A simple valve oscillator V, figure 1, was allowed to give a current of some 15 mA. through capacitance K, a variable self-inductance L_1, a coil or coils of self-inductance L_2 linked with the secondary circuit, a coil B supplying energy to the beating circuit described below, a resistance box R_1 and a standard 10-ohm non-inductive resistance. The primary of a Campbell mutual inductometer could at any time be switched into the circuit.

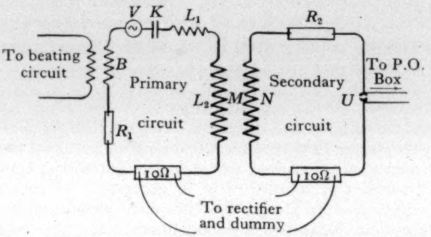


Figure 1. Simple circuit for absolute measurement of resistance.

The anode circuit of the oscillating valve (Mazda P 220) had adjustable capacitance including a variable 0·001-μF. condenser. The inductance L_2 consisted of one or two twin coils of self-inductance 0·15 H., resistance 15 Ω, turns 500 and mean diameter 35 cm. The total effective inductance of the circuit was approximately neutralized, for the frequency used, by the capacitance K.

The secondary circuit. The secondary circuit included a coil N of 67 turns of s.w.g. 18 insulated copper wire about 31 cm. in diameter and of self-inductance 3242 μH. The coil had a maximum mutual inductance of 10500 μH. with either of the twin coils L_2 of the primary circuit. The rest of the circuit consisted of a non-inductive resistance box R_2 adjustable to $0{\cdot}01\,\Omega$, a standard non-inductive 10-Ω resistance similar to that in the primary circuit, and a plug key U which could be either closed to complete the secondary circuit or opened to permit connection with an accurate Post Office box, so that the total resistance S of the circuit could be measured. At any time the secondary of the Campbell mutual inductometer in series with a telephone could be included in the circuit.

---

* Cf. S. G. Starling, *Magnetism and Electricity*, pp. 359–61 (4th edition); A. Gray, *Absolute Measurements in Magnetism and Electricity*, pp. 251, 252; J. H. Jeans, *Electricity and Magnetism*, pp. 465, 466 (4th edition).

The equal-amplitude tester. The 10-Ω coils in the primary and secondary circuits were those of an accurate non-inductive ratio box and were connected, via potential leads, to a mercury rock-over key enabling either to be shunted at will by a circuit consisting of 500 Ω, a full-wave instrument-type Westinghouse metal rectifier (specified as 4-1-1, 50 mA. Inst. unit) and a unipivot 0–120 d.-c. millivoltmeter. Equality of amplitude was judged by identity of deflection of the millivoltmeter as viewed through a microscope with an eye-piece scale on very quickly rocking over the switch, such identity of deflection having been carefully verified when the 10-Ω coils were in series in the same circuit.

As the Westinghouse shunt circuit is not of infinite resistance, and as the primary and secondary currents are interdependent and have circuits of unequal impedance, special precautions have to be taken in accurately judging identity of current-amplitude. For the actual operation of the rock-over will very slightly modify the currents, and this effect, though small, is not symmetrical. Accordingly a dummy circuit of 1650-Ω resistance was prepared and was always switched on to the primary 10 Ω when the secondary 10 Ω was on the Westinghouse circuit, and likewise always rocked on to the secondary 10 Ω when the primary 10 Ω was on the Westinghouse circuit. This dummy resistance was that of the Westinghouse circuit for the order of the deflection used and was such that the resistance of the secondary circuit, even when small, was the same whether the 10 Ω in this circuit was shunted by the dummy or by the Westinghouse arrangement. This equality of resistance was judged by means of a P.-O.-box test with such a direct current, in either direction, as would produce the standard millivoltmeter deflection when the battery key was depressed.

Though this compensating device is most satisfactory it is no longer necessary if the voltages tapped off the 10-Ω coils are switched in turn to the filament and grid of an amplifying valve, the anode current of which is passed through a transformer and thence to the Westinghouse circuit with added resistance. Rectifier M.B.S. 10 is now sufficiently sensitive.

The visible-beater. The output transformer from a valve-maintained tuning-fork was connected to a coil P_1, figure 2, forming an adjustable mutual inductance with a secondary S_1. Likewise the output from the coil B, figure 1, in the valve oscillator primary circuit was led to a coil P_2, figure 2, forming an adjustable mutual inductance with the secondary S_2. The secondaries S_1, S_2 were connected in series through a resistance box R, having a telephone T across it, to a Westinghouse metal rectifier W and a unipivot 0–120 d.-c. millivoltmeter MV. If desired a push-pull wireless transformer having two equal primaries and a common secondary may be substituted for the coils P_1, P_2, S_1, S_2, provided the inputs into the primaries are under control.

If the frequencies of the fork and valve-oscillator current are sufficiently near one another, beats may be heard in the telephone T and seen by the oscillations of the millivoltmeter pointer and so may be counted by both ear and eye. As the variable condenser on the oscillator is turned to bring the frequencies more closely into unison the beats become too slow to be recognized by ear, but the pointer oscillations increase in amplitude and are easily timed by eye. If the steady millivoltmeter deflections, due to each source separately, are made approximately equal at a quarter-scale reading, elegant full-scale swings of the pointer of many seconds' period may be produced when both sources are in operation, and the final tuning to unison is remarkably exact.

If both input circuits are derived from valve-maintained forks whose frequencies are very approximately in simple ratio to one another, beats between the common harmonic components of the currents in the driving circuits, though of small amplitude, are readily seen and counted. Thus a König C 256 fork gave rise to beats of period 3·7 sec. when used in conjunction with a König E fork of frequency
x
$320 + x$. These beats are between the current harmonics of frequencies 5×256 and $4 \times (320 + x)$ and were suppressed by a very minute load upon the E fork. A rapid and accurate check on the relative frequencies of the forks used can thus be easily effected, and data are given in table 5 below.

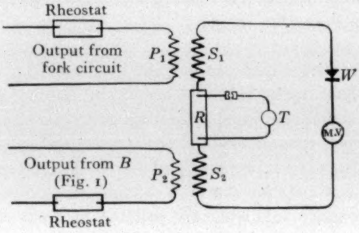


Figure 2. The visibly beating circuit.

§ 3. EXPERIMENTAL TESTS (METHOD 1)

In performing an experiment the capacitance K, figure 1, was adjusted so as to neutralize approximately the total inductance of the primary circuit for the frequency used, while the anode condenser of the oscillator was chosen to produce visible beating with the standard valve-maintained fork, these adjustments being successive.

The resistance of the secondary circuit was set to produce an induced current approximately equal to the primary current, the final exact adjustment being made after tuning the oscillator to beat with the fork not more than once a minute. Any slight drift of frequency was easily corrected by a slight turn of the anode 0·001-μF. condenser.

As soon as currents of equal amplitude, as judged by several rock-overs, had been obtained, the oscillator was switched off and the resistance of the secondary circuit was measured on a reliable Post Office box after removal of the plug key U, the resistance of the leads (as taken when the plug key was inserted) having been adjusted previously to an exact number of hundredths of an ohm. Whether the secondary 10Ω was shunted by the dummy or by the Westinghouse circuit the value of S thus obtained was in all cases the same to the nearest 0·01 Ω.

The mutual inductance M between the primary and secondary was then measured with a Campbell mutual inductometer, the primary of which was switched into the primary circuit while the secondary and telephone were inserted in the secondary circuit. The usual impurity device was included and the frequency was maintained, by adjusting capacitance, at approximately that of the fork.

The self-inductance N of the secondary circuit is of smaller importance than M and was practically constant throughout the experiments. It was measured twice with the Heaviside-Campbell equal ratio bridge and found to be 3242 μH.

Variation of M for further tests was obtained by using one or both of the twin coils L_2 and by separating L_2 and N. As the range of the inductometer was limited to 11,100 μH. it was necessary when working above this range to add to it, at sufficient distance of separation, a 10,000 μH. standard of mutual inductance which could readily be cross-checked against the inductometer.

The results in tables 1 to 5 form a continuous series obtained when the mains were used with an eliminator as a source of high tension for the oscillator. Even in spite of slight fluctuations due to the d.-c. mains the equal-amplitude tester was very sensitive to changes of secondary resistance, which affect the primary and secondary currents in opposite directions. A change of ± 0·02 Ω clearly upset the equilibrium when the secondary resistance was some 25 Ω, and a change of ± 0·05 Ω did so when the value of the secondary was 67 Ω. We found later that if a high-tension battery was substituted for the mains and eliminator perfect quiescence was obtained, allowing a higher-power microscope to be used and aiding the ease and certainty of the equal-amplitude setting. Under such circumstances a secondary resistance of 32 Ω could be set by the tester to within ± 0·01 Ω.

Tables 1, 2, 3 and 4 give data for the four frequencies used. S is calculated from the relationship $S = 2\pi n\sqrt{(M^2 - N^2)}$ after M and N have been expressed in centimetres by multiplying the readings in microhenries by 10^3. Table 5 gives the

Table 1. Results when $n = 512$, $N = 3242$ μH.

M (μH.)	$S \times 10^{-9}$ (c.g.s.u.)	Resistance by bridge (Ω)
21090	67·04	67·09
18629	59·02	59·07
16626	52·46	52·50
10557	32·32	32·31
10510	32·16	32·14
8067	23·76	23·73
6025	16·34	16·30$_5$

Table 2. Results when $n = 384$, $N = 3242\,\mu$H.

M (μH.)	$S \times 10^{-9}$ (c.g.s.u.)	Resistance by bridge (Ω)
21087	50·27	50·21
18790	44·66	44·66$_5$
16695	39·51	39·49$_5$
13608	31·89	31·87
10578	24·29	24·29
8085	17·87	17·88

Table 3. Results when $n = 320$, $N = 3242\,\mu$H.

M (μH.)	$S \times 10^{-9}$ (c.g.s.u.)	Resistance by bridge (Ω)
10553	20·19	20·25
21097	41·91	41·87
18757	37·15	37·17
16718	32·97$_5$	32·96$_5$
13703	26·77	26·79

Table 4. Results when $n = 256$, $N = 3242\,\mu$H.

M (μH.)	$S \times 10^{-9}$ (c.g.s.u.)	Resistance by bridge (Ω)
21067	33·48	33·51
18651	29·54	29·60
16634	26·24	26·26
13615	21·27	21·29
10746	16·48	16·50
10746*	16·48	16·47

* A second König fork, 256 B, was used in this experiment.

Table 5. Beats produced by valve-maintained tuning-forks

Beating* forks	Interval	Frequency of common octave	Time occupied by 10 beats in seconds	Corrected frequency of second fork
256 & 320	major third	1280	37	320·07
256 & 384	fifth	768	50·5	384·10
256 & 512	octave	512	88	512·11
256 & 256 B	unison	256	123	256·08

* The second fork in all cases required load for perfect harmony.

beats between the 256 fork and the others: the corrected value of the higher fork is relative only, the 256 fork being assumed to be correct. Such corrections have been neglected in the calculation of S.

§4. METHOD 2: A SIMPLE FORM OF CAMPBELL'S TWO-PHASE ALTERNATING CURRENT METHOD OF MEASURING RESISTANCE

If the arrangement shown in figure 1 be modified so as to take the form shown in figure 3 we have a circuit which is of value in teaching Campbell's method[*] of determining the ohm, and experiments may be carried out with a current of 15 mA. derived from a simple valve oscillator.

The primary circuit now includes the primary P' of a variable mutual inductance, preferably that of a Campbell mutual inductometer. The secondary circuit has two additions, viz. the resistance R whose magnitude is required, with potential leads, and the phase-adjuster consisting of a capacitance K' in parallel with a variable non-inductive resistance R_3 which permits of fine adjustment. The object of this multiple-arc arrangement is to neutralize the small self-inductance N of the secondary circuit so that the induced current shall be in quadrature with the primary current as well as ultimately equal to it in amplitude. Such compensation is attained when $N = R_3^2 K'$ approximately and is almost independent of frequency, which only slightly influences the equivalent resistance. As the inductance-neutralizer introduces effective resistance into the circuit, and as the secondary current is limited when equal to the primary by the relationship

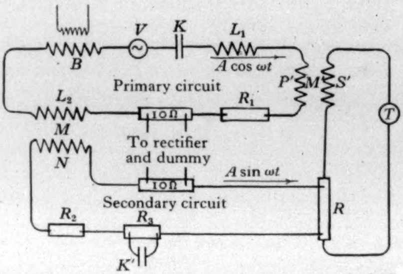


Figure 3. Simple form of Campbell two-phase alternating current method of measuring resistance.

$$S = 2\pi n M$$

(N being now zero), it is well to use as a standard of frequency a valve-maintained fork of frequency not less than 512, and to set M at its largest value (in our case 21,000 μH.). The resistance R is connected to the telephone T and the secondary S' of the mutual inductometer.

If by adjusting the mutual inductance M' silence can be obtained in the telephone when the primary and secondary currents are in quadrature as well as equal in amplitude, we have Campbell's relationship

$$R = 2\pi n M' \qquad ......(4).$$

---

[*] A. Campbell, *Proc. R. S.* **81**, 450 (1908); **87**, 398 (1912). For a brief account see the *Dictionary of Applied Physics*, **2**, 224, 426.

In performing a first experiment the capacitance K in the primary circuit and the oscillator condenser were adjusted successively, as in § 3 above, to neutralize approximately the primary inductance and to produce visible beats with a valve-maintained König fork of frequency 512. The resistance R was one of the 10-Ω ratio arms of a Post Office box. K' was about 2 μF. and the resistance R_3 was adjusted until, irrespective of equality of amplitude of the two currents, a reasonably sharp inductometer balance, as judged by approach to silence in the telephone T, was obtained. This occurred when R_3 was about 40 Ω and it showed the close approach to perfect quadrature, the secondary circuit being approximately non-inductive. The primary and secondary currents were now adjusted to equality with the box R_2, as judged by the equal-amplitude tester, the frequency was controlled to obtain visible beats not exceeding one a minute, and R_3 was slightly adjusted for sharpness of inductometer-telephone balance. The adjustments were successive. A sharp reading for M' was thus obtained without the slightest difficulty, and a zero reading, equally sharp, was taken similarly with the 10-Ω plug of R inserted.

By making K' about 2·3 μF., R_3 was reduced to some 38 Ω, permitting R to be increased to 20 Ω while leaving sufficient surplus secondary resistance to allow of equal-amplitude adjustment with the box R_2. Table 6 shows the readings obtained.

Table 6. Determination of resistance by Campbell's method

$$n = 512, \quad R = 2\pi n M'$$

Nominal value of R	K' (μF.) approx.	R_3 (Ω) approx.	M' (μH.)	$R \times 10^{-9}$ (c.g.s.u.)	Resistance as measured with bridge (Ω)
zero (plugs inserted)	2	40	zero (by zero adjuster)	—	zero (lead reading taken)
10 Ω (left arm)	2	40	3101	$9{\cdot}97_6$	9·98
10 Ω (right arm)	2	40	3102	$9{\cdot}97_9$	9·98
20 Ω (both arms)	2·3	38	6208	19·97	19·96

§ 5. CONCLUDING REMARKS

The experiments described in this paper may be simplified and readily performed by advanced students. Inexpensive condensers may be used for capacitance in both methods. If no inductometer is available, the fundamental relationships involved in the methods, viz. those of equations (1) and (4), may be tested by resorting to the Owen and Carey Foster bridges for the measurements of self and mutual inductance respectively, though the absolute character of the methods is thereby sacrificed.

By virtue of the high inductance of the primary circuits, which ensures that the currents are minute until neutralizing capacitance for the fundamental frequency is introduced, error due to the presence of harmonics appears to be very small and inductometer balances are sharp.

§ 6. ACKNOWLEDGMENTS

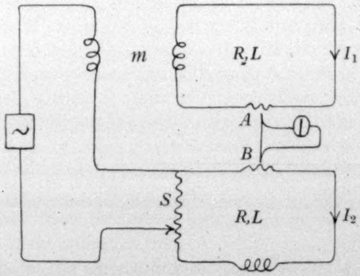
We express our gratitude to Prof. A. Griffiths who has generously provided us with apparatus and to Dr D. Owen, of the Sir John Cass Technical Institute, for the loan of a variable self-inductance. We thank Mr W. Wilson, Mr S. Baker and Mr R. Edgerton of the Physics Department, Birkbeck College, for suggestions and for assistance in our measurements.

DISCUSSION

Dr D. OWEN. The authors' first method utilizes ingeniously the fact that in the a.-c. transformer there is a simple relation between the resistance of the secondary, the mutual inductance, the self-inductance of the secondary, and the frequency, if the primary and secondary currents are exactly equal. From this relation the resistance of the whole of the secondary circuit may be calculated in absolute measure. It must be borne in mind that the effective a.-c. resistance of a coil is not equal to its d.-c. value, but always in excess of it, to an extent increasing with the frequency. It would have been of interest if results for the same circuit at various frequencies could have been recorded. The second method furnishes a simple means of carrying out A. Campbell's a.-c. determination of absolute resistance, which may with advantage be included in the laboratory course of the advanced physics student.

Mr A. CAMPBELL. The authors' second method is quite suitable for an ordinary laboratory and the results show that it can give good accuracy. Some time ago I introduced a somewhat similar system as a phase-splitter for a.-c. potentiometers[*]. It is rather simpler in detail than that of the authors, but not so self-contained for students' use.

In the accompanying figure the two loops have equal total resistance R and self-inductance L, being set by preliminary tests. The currents I_1 and I_2 will thus be always in quadrature. By means of differential thermo-junctions and heaters A and B, by altering either S or m, we can get



$$I_2 = I_1.$$

---

[*] British Patent Specification No. 342,441.

Then $$S = \omega m = 2\pi n m,$$
which determines the resistance S in terms of m and n. With ordinary apparatus I have obtained accuracy to about 1 part in 2000.

I have suggested the system to Dr Hartshorn as an alternative to my *M-R* method, by which the National Physical Laboratory has recently made a determination of the ohm. It is sufficiently sensitive and requires very little apparatus, but it has one weak point—the accuracy is lowered by the presence of harmonics, for balance is obtained by making the effective (r.m.s.) values of I_1 and I_2 equal, and not, as in the *M-R* method, by use of a selective vibration galvanometer.

AUTHORS' reply. In reply to Dr D. Owen: We hope to carry out shortly further tests on the absolute measurement of resistance by a yet more simple a.-c. method. We shall certainly keep his suggestion in mind and measure the same resistance under different frequencies.

We are very interested to learn that Mr Albert Campbell has used a simple device in which two currents, always in quadrature, are adjusted to equality to enable a resistance to be measured absolutely in terms of a mutual inductance and a frequency. The circuit of figure 3 is designed for teaching purposes to resemble the original arrangement as closely as possible and it is perhaps an advantage that the student has to perform the adjustment for quadrature carefully to obtain sharpness of balance.

538.54

THE DEMONSTRATION OF EDDY CURRENTS IN CONDUCTORS OF VARIOUS SHAPES

By D. BROWN, Ph.D., Auckland University College,
New Zealand

Received March 13, 1933. *Read and demonstrated, in the absence of the author, by Prof. P. W. Burbidge, May* 19, 1933

ABSTRACT. In this paper a method is described whereby it is possible to demonstrate visually the existence of eddy or Foucault currents in masses of conducting material, and the way in which the flow of the currents may be distorted or baffled by suitable slots or laminations. The experiment is very easy to set up, and would make a good conversazione experiment.

In the teaching of electromagnetic induction, demonstrations of the existence of eddy currents are usually of an indirect character, involving the resistance to motion of a mass of metal in a magnetic field or the rise in temperature of the metal. It is thought that the following method enables the eddy currents in metal specimens to be demonstrated more directly.

The specimens were made out of brass or copper sheet $\frac{1}{4}$ in. thick and cut into various shapes, and the currents were induced in them by placing them in the field of a vertical a.-c. electromagnet with a laminated iron core. A horizontal insulating platform of glass or ebonite was supported about 2 in. above the top of the electromagnet and the specimens were laid on this so as to be cut more or less normally by the field. A sheet of cardboard, or better still opal glass, sprinkled with very finely divided (for instance, ground) iron was then laid on the top of the specimen.

The use of iron filings in connexion with static fields is, of course, a commonplace, but when used with a.-c. fields they give effects which are much more striking, as the particles forming the pattern are observed to be in continual motion which may take the form of either a violent oscillation or a slow circulation round a closed contour. In the present case the particles are in an alternating field which is partly due to the eddy currents and partly due to the exciting magnet, but it is at once seen that they form themselves into a moving pattern which is closely related to the shape of the specimen used.

Thus figure 1 shows the pattern due to a circular disc 4 in. in diameter and that due to the same disc after it has been slotted with five radial saw-cuts extending half-way in towards the centre. The clear spaces between the arms of this pattern coincide with the radial slots, and the current evidently flows round the slots, while the large peripheral current is very much reduced. The particles in each arm of the pattern exhibit the slow circulation effect referred to above. This is shown to an altogether greater extent, however, by the use of a specimen in the form of a cross, figure 2. The boundary portion of this figure consists partly of isolated particles which are in a state of rapid radial oscillation, and partly of upright needle-shaped aggregates which exhibit no oscillation but gravitate steadily towards the arms of the cross. There they unite to form a continuous stream moving in towards the centre, but as they move the mutual repulsion between adjacent needles keeps them spaced

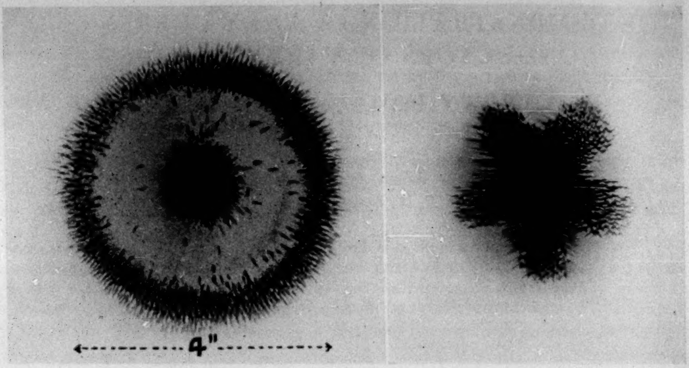


Figure 1.

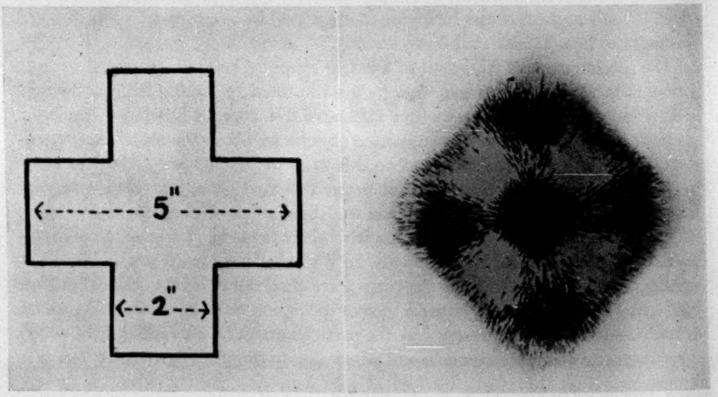


Figure 2.

out like the bristles on a brush. The centre of the pattern is crowded with needles mainly under the control of the exciting field, but the strong mutual repulsion is continually pushing individual members towards the edge of this group, where they become equally affected by both the exciting and the induced fields. These fields are not in phase, so that the needles acquire a violent quivering motion which eventually disintegrates them into a powder which flies out to rejoin the boundary curve. In this way a continual circulation is kept up as long as the field is switched on, and there is no tendency for the material to accumulate at any one point. The resulting pattern represents an equilibrium effect, which may be varied considerably by altering the frequency or the strength of the exciting field.

Although a great variety of results can be produced by experimenting, they can usually be explained by bearing in mind certain governing factors. If we consider the circular disc of figure 1, for obvious reasons the eddy currents will be strongest near the rim of the disc, and the field they produce is the main influence acting upon the outer ring of particles. The central group is controlled by the exciting field, and in between there is a neutral region where neither field can predominate. The power factor for the eddy currents will be nearly unity, and the field they produce will be a minimum when the exciting field is a maximum, and *vice versa*. The powder in the outer ring is thus urged inwards and outwards alternately, and in fact a boundary of this character is found round any specimen in which a large peripheral current is permitted.

There is a certain exchange of particles which goes on between the inner and outer regions, but this exchange assumes much greater proportions in the case shown in figure 2, and it is interesting to see how it is maintained. The relatively clear spaces in this pattern are traversed by an outward streaming of powder produced by the disintegration of the central cluster as previously described, and it is rather surprising that this stream moves uniformly outwards without appearing to be affected by those half-cycles in which the exciting field predominates. The cause of this is probably the increased friction which arises between the particles and the surface during these half-cycles owing to the large downward component of the force exerted on them. When the eddy-current field predominates its action is almost entirely horizontal and the particles are always able to profit by it.

Once the particles have united, however, to form an upright needle they appear to respond much more readily to the exciting field, and one finds (for example in the first pattern of figure 1) a few needles advancing inwards in the face of a stream of powder flowing outwards. A needle seems to be able to behave in this way owing to the fact that its magnetic moment when it is saturated is large in the direction of the exciting field and small in the horizontal direction, so that the eddy field is able to get but little grip on it, and the smallness of the base of the needle makes the frictional resistance less important.

The ability of the smaller particles to ignore the exciting field ceases when they reach the boundary of a figure, and there they oscillate violently backwards and forwards. The divergence of the exciting field may cause it to have an increased horizontal component in these regions, and the frictional factor is lessened owing to the action being so violent here that the particles are in contact with the surface for only a part of the time.

Whenever a peripheral current in a specimen is large enough to maintain a boundary curve in the pattern, the process of exchange between the inner and outer regions appears to take place. Thus, even with the slotted disc of figure 1, if the slots are made shorter (for instance, one third of the radius) the pattern acquires a circular boundary and a circulation like that described for figure 2 ensues.

The a.-c. magnet employed had an iron core 2 in. in diameter and took about 80 watts at 230 volts; the frequency of the alternating current was varied from 40 to 60 ~. An ordinary electromagnet with a solid core could probably be used for short periods. Ordinary iron filings do not seem to be suitable for the experiments; a finer type of particle is required. As specimens for showing circular eddy currents a set of rough brass weights served excellently, and doubtless many other variations will occur to any experimenter.

DISCUSSION

Dr L. F. Bates said that modern magnetic alloys gave better results in experiments of this kind than the traditional iron filings. After reading the paper he had tried the experiment with mu-metal dust and obtained good results; but he had obtained a still more striking improvement by mixing mu-metal dust with iron filings.

535.338:546.57

THE ABSENCE OF FINE STRUCTURE IN THE ARC SPECTRUM OF SILVER

BY S. TOLANSKY, PH.D., 1851 Exhibition Senior Student,
Imperial College of Science, London

Communicated by Prof. A. Fowler, F.R.S., April 5, 1933.
Read in title May 19, 1933

ABSTRACT. The arc spectrum of silver, produced in a water-cooled hollow-cathode discharge, has been examined for fine structure with a variable-gap silvered Fabry-Perot interferometer in the region 8300 to 4000 Å. Results for the resonance lines at approximately 3300 Å. are also quoted. Silver consists of two odd isotopes 107, 109, and although 5*s*, 6*s*, 7*s*, 5*p*, 6*p*, and 5*d* terms have been studied no trace of fine structure has been found, in spite of very excessive over-exposing in many lines. All lines are extremely sharp and are worth considering as wave-length standards, being well distributed. Attention is drawn to the fact that the analogous spectrum of Cd II also shows no fine structure, so that it is concluded that the absence of structure is probably due to the electron configuration and not necessarily to smallness of the nuclear magnetic moment. This is remarkable, for penetrating *s* electrons are involved in some configurations.

§1. INTRODUCTION

A NUMBER of previous investigators have examined the important lines of the arc spectrum of silver* for fine structure. In no case, however, have both the source and the interferometers been such as to give very high resolution, so that a thorough re-examination of the spectrum has seemed desirable. The atomic weight of silver is 107·88, and as Aston† has shown that there are two odd isotopes 107, 109 the calculated abundance ratio is 1 : 1 if the mass defect is taken approximately as about 0·13, which, from the position of silver on the mass curve, is what it will roughly be. As both the isotopes have odd atomic weights it is natural to assume that they possess nuclear spins. Many terms of the silver arc spectrum involve deeply penetrating electrons, so that according to expectations the spectrum should show fine structure due to nuclear spin. No evidence of fine structure, however, has been found. The mass isotopic shift will be far too small to be observable and need not come into consideration.

§2. EXPERIMENTAL RESULTS

The spectrum was excited in a hollow cathode of silver, some 40 mm. long and with an 8 mm. bore. Helium was continually circulated through the tube at an approximate pressure of 1 mm. and as the gas passed through a charcoal trap immersed in liquid air, a high degree of purity was maintained. The tube was excited by means of a small generator supplying 1000 volts d.c., and currents of either 200 or 300 mA. were used. The cathode was cooled with a continuous water flow. With this arrangement the tube radiated only the helium lines and the silver arc spectrum, the lines of the latter being very intense and very sharp indeed.

---

* S. Frisch, *Z. f. Phys.* **71**, 59 (1931), etc.

† *Proc. R. S.* A, **115**, 487 (1927).

Since most of the important silver arc lines (excluding the resonance lines) lie in the infra-red and visible portions of the spectrum, a silvered Fabry-Perot interferometer was used to examine the lines for fine structure. The interferometer was the Hilger N 71 and was crossed with a large glass two-prism spectrograph of big aperture, the dispersion of which was about 30 Å. per mm. at 5000 Å.* The largeness of the apertures of both spectrograph and interferometer resulted in a very fast combination.

The interferometer was silvered by the evaporation process described by R. Ritschl†, the acid after-treatment being carried out in detail. In the blue and violet regions Ilford Monarch plates, in the green and red Ilford Hypersensitive Panchromatic plates, and in the infra-red Ilford Infra-red Sensitive plates were used‡. Exposure times varied considerably, the green lines being so intense that one to two minutes sufficed for normal exposure, but the infra-red lines required an hour. Photographs extending up to four hours were taken for all regions so that faint components should not be missed.

The line transitions which have been observed are shown in figure 1. The two ultra-violet resonance lines could not be studied, but the author has had the privilege of examining photographs of these lines taken with 25- and 35-plate reflection échelons by Mr W. E. Williams of King's College, London.

The term scheme in figure 1 shows that the following terms come into consideration.

$$\begin{array}{lll}
5s\ {}^2S_{\frac{1}{2}} & 6s\ {}^2S_{\frac{1}{2}} & 7s\ {}^2S_{\frac{1}{2}} \\
5p\ {}^2P_{\frac{1}{2}} & & \\
5p\ {}^2P_{\frac{3}{2}} & & \\
5d\ {}^2D_{\frac{3}{2}} & 6d\ {}^2D_{\frac{3}{2}} & \\
5d\ {}^2D_{\frac{5}{2}} & 6d\ {}^2D_{\frac{5}{2}}. &
\end{array}$$

One of the terms is involved seven times, one five times; five are involved twice and the remaining two once, so that there is ample opportunity for checking conclusions as to term structures.

All the lines which have been examined are given in the table, the allocations being those given by Blair§. Five of the observed lines have not yet been allocated||.

---

* The spectrograph was that bequeathed to the Royal College of Science by the late Col. Gifford.

† *Z. f. Phys.* **69**, 578 (1931).

‡ The author is indebted to Dr Bloch of Messrs Ilford Ltd., for supplying him with a new type of plate not yet marketed. This plate is very fast and as it needs no ammonia sensitization is entirely free from fog.

§ *Phys. Rev.* **36**, 1531 (1930).

|| H. Kayser, *Handbuch der Spektroscopie*, Bd. **7**, gives a close neighbour to 4620·0 Å.

Table

Wave-length	Classification	Wave-length	Classification
8273·7	$5p\ ^2P_{\frac{3}{2}}$–$6s\ ^2S_{\frac{1}{2}}$	4476·1	$5p\ ^2P_{\frac{1}{2}}$–$7s\ ^2S_{\frac{1}{2}}$
7668·1	$5p\ ^2P_{\frac{1}{2}}$–$6s\ ^2S_{\frac{1}{2}}$	4311·1	
5471·5	$5p\ ^2P_{\frac{3}{2}}$–$5d\ ^2D_{\frac{3}{2}}$	4212·7	$5p\ ^2P_{\frac{3}{2}}$–$5d\ ^2D_{\frac{3}{2}}$
5465·5	$5p\ ^2P_{\frac{3}{2}}$–$5d\ ^2D_{\frac{5}{2}}$	4210·9	$5p\ ^2P_{\frac{3}{2}}$–$5d\ ^2D_{\frac{5}{2}}$
5209·1	$5p\ ^2P_{\frac{1}{2}}$–$5d\ ^2D_{\frac{3}{2}}$	4085·9	
4874·1		4055·3	$5p\ ^2P_{\frac{1}{2}}$–$5d\ ^2D_{\frac{3}{2}}$
4848·1			
4668·5	$5p\ ^2P_{\frac{3}{2}}$–$7s\ ^2S_{\frac{1}{2}}$	3382·9	$5s\ ^2S_{\frac{1}{2}}$–$5p\ ^2P_{\frac{1}{2}}$
4620·0		3280·7	$5s\ ^2S_{\frac{1}{2}}$–$5p\ ^2P_{\frac{3}{2}}$

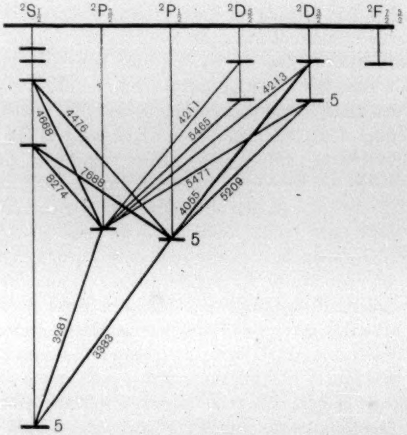


Figure 1. Transitions observed in the arc spectrum of silver.

The instrumental resolution between 4400 and 4000 Å. is not, of course, so good as that for the longer wave-lengths, but it is still quite good enough to show effectively whether appreciable structures exist. The lines were examined with interferometer gaps up to 25 mm. but in no case was any trace of structure found. Indeed, the lines were so sharp that it was not considered that an increase in the interferometer plate-separation would serve any purpose whatever. A number of the lines were also very heavily over-exposed, but no faint components were seen. It is quite certain that all the lines observed are single, and furthermore are so extremely sharp, bright, and well distributed that they could be used as wave-length standards with considerable advantage*.

---

* The line $5p\ ^2P_{\frac{1}{2}}$–$6s\ ^2S_{\frac{1}{2}}$ is somewhat broad, and a very narrow doubling is suspected. This would be due to $6s\ ^2S_{\frac{1}{2}}$.

The resonance lines are difficult to produce free from self-absorption effects. The lines photographed by Mr Williams were produced in a water-cooled hollow-cathode discharge, but the cathode was an alloy containing 5 per cent silver and 95 per cent cadmium. The object was to reduce the self-absorption of the silver lines as much as possible without making them unduly weak. The lines are definitely broadened but show no other sign of structure, and it is very probable that the broadening is due to partial self-absorption. If any structure exists it is certainly considerably less than 0·050 cm^{-1}.

It is therefore concluded that none of the observed lines of the silver arc spectrum shows any appreciable fine structure at all.

§3. DISCUSSION OF RESULTS

Before discussing the peculiar absence of fine structure we may first call attention to the work of Wali Mohammad and Sharma* on the silver resonance lines. These authors claim to have found that both lines have almost exactly the same fine structure, namely two strong components 0·218 cm^{-1} apart and a faint component about five times less intense further towards the violet. It follows from this that the structure of the resonance lines is the same as the structure of the $5s\ ^2S_{\frac{1}{2}}$ term. On theoretical grounds this is quite impossible, for the maximum possible number of components is two, since the term multiplicity is $2J+1$ and $J=\frac{1}{2}$. Even with the assumption that an isotope displacement effect produces the structures four components should result, and the intensities would be quite different, the maximum possible intensity-ratio of any pair of components never exceeding 3·0 : 1. In the event of the nuclear magnetic moments being such that the weaker components fall together there should be three lines with intensities in the ratio 3 : 3 : 2, so that every possibility is theoretically excluded.

When the observations of Mr Williams are taken into account it is quite obvious that the reported structure is nothing more than a case of self-reversal. The fact that two equally intense components result (together with the faint line) is evidence of this. None of the components appears in the water-cooled hollow cathode. The source used by Wali Mohammad and Sharma (a vacuum arc) is much more liable to produce reversal.

As regards the present observations, it will be seen that these are very difficult to explain. It is quite certain that silver consists of two odd isotopes and both should possess nuclear spins; for every odd atom so far investigated has been shown to have a nuclear mechanical moment, although the nuclear magnetic moment may be small. The terms examined are produced by the $5s$, $6s$, $7s$, $5p$, $6p$, and $5d$ electrons. The first three of these are penetrating electrons and the fourth may be considered as partly so, because the separation between the $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ terms is 203 cm^{-1}. This large gross-structure multiplet separation would suggest that the coupling between I and J should be large. It follows from this that, if the silver nucleus possesses an average nuclear magnetic moment, i.e. if the $g(I)$

---

* *Ind. J. Phys.* **6**, 75 (1931).

factor is not abnormal, measurable fine structures are to be expected, particularly in the *s*-electron terms.

The absence of structure can only be attributed to one of two causes; either (1) the nuclear magnetic moment is small, or (2) the coupling between the nucleus and all the external electrons, even penetrating *s* electrons, is small. With reference to these two points, attention is drawn to some unpublished results of Mr E. G. Jones on the spectrum of Cd II. This spectrum is analogous to that of Ag I, the two spectra being in fact, in iso-electronic sequence, and Jones has observed terms practically identical with those reported here for Ag I. In no line has any fine structure been found. As the Cd I spectrum shows very wide fine structures in suitable terms, the cadmium nucleus must possess a large nuclear magnetic moment, Jones concludes therefore that the absence of structure in Cd II must be entirely due to the electronic configuration, or else to some nuclear change in the process of ionization. The latter is highly improbable, judging from work on bismuth and like elements. If the electron configuration of Cd II is such as not to produce fine structures, the same should hold true for Ag I. This fact is very surprising indeed, for, as has been pointed out, penetrating *s* electrons are involved in many terms, and in others the gross structure multiplets are wide.

Any conclusions made about the $g(I)$ factors of nuclei must be carefully considered in the light of the present observations. It appears that the presence of penetrating electrons or large gross-structure multiplets is not evidence enough for assuming that the coupling between J and I will be large. It has always been previously assumed that penetrating *s* electrons will give easily measurable structures, but the present facts contradict this assumption. It may be observed, too, that the extreme sharpness of the Ag I lines shows that no isotopic displacement effect exists.

§4. ACKNOWLEDGMENTS

The author wishes to express his thanks to Mr W. E. Williams and Mr E. G. Jones for permitting the use of unpublished data. His thanks are due to Prof. A. Fowler, F.R.S., for encouragement and help.

DISCUSSION

Prof. A. O. Rankine said that confusion was likely to arise between the symbols for silver iodide and the neutral silver atom, both being denoted by Ag I. Would it not be better to write Ag.I for the atom?

Dr W. Jevons. The observations of the lines λλ 3281 and 3383 to which the author refers are described in a letter by W. E. Williams and A. Middleton in the current number of *Nature*, which also contains a letter by D. A. Jackson recording similar observations of these two lines and five others of neutral silver*. Both investigations agree with the author's in denying the existence of fine structure such as has been reported by other observers using an unsuitable source. I would like to endorse the President's remarks about the unsatisfactory nature of the symbols which are very widely used to denote emitters of line spectra. Many besides chemists have been misled by the representation (especially in the titles of papers) of a neutral atom M by the notation MI which should surely be reserved for the diatomic iodide. It is true that in many publications care is taken to separate the roman numeral from the chemical symbol by a narrow space, but even this is sometimes not insisted upon. It would be far better to write the numeral in smaller type, either on the same line as the chemical symbol (M I, M II,...), or as a superscript (M^{I}, M^{II},...), or as a subscript (M_{I}, M_{II},...); the first of these alternatives has, indeed, been adopted by many authors, e.g. in the *Astrophysical Journal.* Since it has become known that the successive stages of "simplification" of the atom, which Sir Norman Lockyer first represented by MI, MII, MIII, MIV,..., are the neutral, singly ionized, doubly ionized, trebly ionized,... atom (resulting from the loss of none, one, two, three,... negative electrons), it is a great pity that these symbols are not abandoned in favour of M, M^{+}, M^{++}, M^{+++},..., where the unadorned M represents the neutral atom. This plan has been adopted in the literature of molecular spectra; although the molecules concerned are only neutral and singly ionized, the introduction of such symbols as HClI and HClII for what we denote by HCl and HCl^{+} would have been unfortunate, to say the least. For some atomic emitters the replacement of the usual notation by one of the alternatives mentioned here is particularly desirable; consider, for example, the atoms and atom-ions of iodine and vanadium.

---

* *Nature*, **131**, 691–2 (1933).

AUTHOR's reply. In reply to Prof. Rankine: It is not customary to write a dot between the Ag and the I when referring to the neutral silver spectrum. Instead a space is left, the symbol being written as Ag I. The fact remains that this may still be confused with the symbol for silver iodide, but unfortunately it is the regular practice of most spectroscopists.

In reply to Dr Jevons: The alternative suggestion of writing + signs instead of Roman numerals to designate multiply ionized spectra is used by some authors. The main objection is that the symbol becomes cumbersome with high degrees of ionization, and indeed a visual mistake is easy. Compare for instance the two notations in the case of bromine which has had six electrons removed by excitation, e.g. Br VII and Br^{++++++}.

Dr A. FERGUSON suggested the use of the following more compact notation: Ag, Ag^{+}, Ag^{2+}, Ag^{3+}...Ag^{n+}.

612.843.72:152.7

THE MEASUREMENT OF VISUAL SENSATIONS

BY N. R. CAMPBELL, SC.D., F.INST.P.

Received December 22, 1932, *and in revised form March* 13, 1933. *Read May* 5, 1933

ABSTRACT. The paper is a criticism of Dr L. F. Richardson's proposed method of measuring sensations by "mental estimates". In the absence of agreed principles the discussion is conducted in the light of an analogy with thermometry.

It is argued (1) that Dr Richardson's own facts prove that the method of mental estimates is inferior to another available method of measuring the same thing. If his facts and his implied propositions are true, indirect measurement by means of his *S* must be preferable to direct measurement by *R*. (2) That any arguments that Dr Richardson might base upon the fact that his method of measurement leads to a numerical law between *R* and *S* would be valid only if he proved that this law is true and not empirical. (3) That if his method measures anything, that something is almost certainly not a sensation; at least, that he has provided no evidence that it is a sensation.

Finally it is pointed out that Dr Richardson's method indicates the theoretical possibility of a method of measurement based upon ordering differences of increasing degree; but there is no evidence that the method is ever practically possible.

§ 1. THE PROBLEM

In the discussion on Vision organized by the Physical and Optical Societies on June 3, 1932, of which a report has been issued, the question was often raised whether visual sensations are measurable. But it was never discussed in the light of any general theory of measurement; indeed the only speaker (namely Dr L. F. Richardson, pp. 112–116 of the report) who referred to any such theory (namely my own) deliberately rejected it. The natural conclusion is that physicists generally hold that no general theory of measurement is possible or, at least, that none has yet been established. Of course I do not agree with that conclusion; I think that theories already propounded give a very simple and direct answer to many of the problems that were raised; and that where they fail to provide an answer, the failure lies, not in the theories, but in the ambiguity of the term "sensation." However it would be absurd to consider doctrines in the light of principles that are almost universally rejected; and some other basis must be found for the criticism that I want to offer. Such a basis may perhaps be found in analogy; if we can show that some proposed method of measuring sensations violates conditions that confer its validity on some accepted system of measurement, then we shall clearly throw doubt on the validity of that method.

The only proposed method of measurement that I am going to consider is that of Dr Richardson, though I believe that the arguments advanced have a bearing on the views propounded by other speakers. This method is called by its author that of "mental estimates"; I venture to prefer the simpler term "measurement by guessing." The accepted method of measurement that I shall choose as a guiding analogy is thermometry.

§ 2. THE ANALOGY

If a number of persons dip their fingers into a set of basins of water at different temperatures, each will be able to arrange them, confidently on the whole, but with some doubt in particular cases, in a definite order of warmth; and there will be a strong resemblance between the orders adopted by different observers. Indeed it is probable that it will never happen that one observer declares confidently that *A* is warmer than *B*, while another declares with equal confidence that *B* is warmer than *A*. Further the observers can probably be induced to represent the basins by points on a straight line, the ends of which represent the hottest and the coldest basin, in the manner described by Dr Richardson. The order of these points will, of course, agree to the same extent; and the range covered by the points assigned by different observers to represent the same basin will be much less than the whole length of the line, and not very much greater than that covered by the points assigned to the same basin by the same observer at a number of successive trials separated by an interval so long that memory plays no part.

§ 3. WHY IS THE ANALOGY NOT MEASUREMENT?

But such measurement by guessing is not the standard method of measuring temperature; we do not take *R*, the mean distance of a representative point from one end of the line, as the measure of the temperature of a basin. Why? Dr Richardson would reply, I think: Because we have a better way of measuring temperature; if we had no better way, *R* would measure temperature. Now that answer implies two propositions: (1) that there can be two ways of measuring the same thing; (2) that the purpose of measurement is something in which accepted methods of measurement excel guessing. Further I think he would admit that this something is primarily sensitivity (though he might prefer to call it accuracy). If we compare (say) platinum-resistance thermometry with guessing, the striking difference is that by the former we can distinguish basins that are indistinguishable by the latter; the thermometer can say definitely that one basin is warmer than another, when direct sensation detects no difference at all.

§ 4. MEASUREMENT AS NAMING

If that is so, we can reach our first conclusion. It is that one purpose at least of measurement is to distinguish things. The numerals assigned in measurement are, in part at least, names. In this respect a method of measurement would be ideal if it always led us to assign exactly the same numeral, the same name, to the same object, and always to assign different numerals to objects that are in any way distinguishable in the property we are considering. The second part of this ideal is attainable. For every measurable property there is one most sensitive method of measurement (or possibly a group of such methods all equally sensitive and more sensitive than any other). If we adopt that method, then we shall never assign the same name to distinguishable things; and we have no right to adopt any other method, except for professedly provisional purposes, or to regard it as really constituting measurement. On the other hand, the first part of the ideal is usually unattainable. In all but a small group of measurements, the most sensitive method will sometimes lead us to assign different numerals to the same thing; that is due to what is called experimental error. Accordingly we need not demand that a proposed method of measurement fulfils the first part of the ideal.

§ 5. WHEN ARE TWO MAGNITUDES THE SAME?

We must now return to the proposition called (1) above. What is the criterion by which we are to determine whether two methods of measurement measure the same thing? This question has often been asked; many people seem to find a strange difficulty in answering it. To me the answer seems perfectly clear, and to depend on the conception of order; this conception must be fundamental in measurement, because the obvious reason for giving to numerals a unique position as names is their possession of a very definite and complete kind of order. My answer is that two methods measure the same thing, if the order of the numerals assigned by one to the members of a group is always the same as the order of the numerals assigned by the other to those same members. If, and only if, that is so, there is a definite and significant one-one relationship between the names assigned by the two methods. But one proviso must be added. The orders assigned by two methods differing in sensitivity can never be exactly the same; for one will distinguish things that the other confuses. Unless we are to confine the term measurement entirely to the most perfect methods, and refuse to recognize imperfect methods as measurement at all, we must add that differences of order arising inevitably from the ambiguity of the less perfect methods are negligible. Methods are the same if, and only if, their orders are the same as far as the ambiguity inherent in any of them permits.

According to this criterion platinum thermometry and guessing measure the same thing (subject to certain reservations raised in § 8, which enforce our ultimate conclusions). But let us carry our analogy with Dr Richardson's work a step farther, and suppose that the basins are prepared by mixing in them S parts of hot water with $100-S$ parts of cold water, S being measured. The order of R, the numeral assigned by guessing, will be found to agree, apart from ambiguity, with the order of S. If R is plotted against S a smooth curve will be obtained. But do S and R measure the same thing, according to the criterion? If basins are never prepared otherwise than by mixing the hot and cold water, the answer is, Yes. But we must note two possibilities. (*a*) We might prepare by other means basins of water precisely similar to those produced by mixing, e.g. by heating cold water with a flame. (*b*) We might prepare objects of other kinds, e.g. basins of oil or even solid bodies, that could not be simulated completely by mixing hot and cold water, and yet could be "measured" in exactly the same way and included in the same order with the basins of water. If we take these possibilities into account, the order of *R* is not always the order of *S*; for there may be no *S*. Accordingly, especially in view of possibility (*b*), we should say that *S* and *R* do not measure the same quantity. But we must note also (*c*) that we could always prepare by mixing hot and cold water, a basin, characterized by a definite *S*, which would be equal in temperature to, and have the same value of *R* as, any of the objects that had not been, or could not be, prepared by that process.

In these circumstances, I think our attitude would be this. *S* and *R* are not the same thing. But by measuring the *S* of a body having the same temperature as a body which can otherwise be measured only by *R* (for the moment we are ignoring platinum and other thermometers), we obtain a more sensitive way of measuring the thing measured by *R*. For *S* is actually less ambiguous than *R*; and the ambiguity in deciding whether two temperatures are equal is less than that in assigning *R*'s to them. Though *R* may be a way, even the only way, of measuring the thing directly, *S* measures it indirectly; and the indirect method is the better; it is to be preferred always, except when we are temporarily content to put up with imperfection.

§ 6. FIRST CONCLUSION

The analogy is incomplete only because, in Dr Richardson's work, possibility (*b*) is absent and perhaps possibility (*a*). (I simply do not know whether a series of differently saturated hues can be prepared otherwise than by mixing a saturated hue with white.) The absence of these possibilities makes it less plausible to maintain that *R* and *S* are not the same thing; but, whether they are or are not the same thing, possibility (*c*) makes it quite certain that measurement by *S*, even if it is indirect, is a better way of measuring what *R* measures than direct measurement by *R*. Our conclusion then is this. Dr Richardson's advocacy of his proposed method of measuring sensations rests on the smooth curve that he obtains between *R* and *S*. But that proves only that *S* and *R* have the same order, apart from ambiguity inherent in *R*. But that, in its turn, gives rise to a strong suspicion that *R* measures the same thing as *S*, so that his proposed method measures a "stimulus," not a sensation; and it proves quite definitely that, even if *R* and *S* are not the same thing, the best way to measure what *R* measures, is *not* by his method, but by the indirect method involving *S*. In other words his facts prove the exact opposite to his conclusion.

§ 7. MEASUREMENT AND NUMERICAL LAWS

So far we have assumed that the purpose of measurement is distinction and identification. And that is certainly one purpose. But if we return to our analogy we shall see that there is another. (If a psychologist reads what follows, he may not understand the references to "fixed points" and "thermodynamic scale"; but he need not understand more than the conclusions drawn.) Platinum-resistance thermometry requires four fixed points. Numerals can be assigned to other temperatures with the same sensitivity and definiteness, whatever numerals are assigned to these points. Actually however we do not regard it as providing satisfactory measurement, unless they are so assigned that the scale agrees with the thermodynamic scale. Why?

The reason is that one of the purposes of measurement is to enable us to discover numerical laws between things measured. Physicists do not regard a law as a true numerical law, unless its form is simple and/or explicable by a theory; if it does not fulfil that condition, it is a mere empirical law. It is a fact that we do not arrive at true, as distinct from empirical, laws involving temperature, unless we choose the fixed points so that the numerals assigned by platinum thermometry agree with the thermodynamic scale.

It appears to me that part of Dr Richardson's arguments in favour of his measurement by guessing (he never states them definitely) are based on this purpose of measurement, the formulation of numerical laws. He argues that his relation between *S* and *R* is a numerical law, and that therefore the process of assigning numerals on which it rests, since it fulfils this purpose of measurement, must be measurement. If he produced any evidence that his law is a true, and not an empirical, law, the argument might have some weight, though it would never be conclusive. But in the absence of that evidence, it is of no value at all. Any process of assigning numerals in respect of a property capable of order, in accordance with that order, can hardly fail to lead to an empirical numerical law relating the property to some other. But the process of assigning numerals in accordance with an order is not necessarily measurement; if it were, the "numbering" of houses in a street would be measurement. If Dr Richardson is going to introduce at all the conception of a numerical law—a distinctively physical conception—he must accept the general standpoint of that science. In physics it is quite certain that a process of assigning numerals is not regarded as measurement, unless it fulfils conditions more stringent than the mere representation of order. The fact that a process leads to a true numerical law may possibly be evidence that these more stringent conditions are fulfilled; the fact that it leads to an empirical law most certainly is not.

§ 8. IS *R* A SENSATION?

So far we have been inquiring whether *R* measures anything. If we had answered that question affirmatively, it would still have been necessary to inquire whether it measures a sensation. A few remarks on this matter may still be made; fortunately some of them are independent of any knowledge of psychology.

If the line along which Dr Richardson's observers are asked to place their points is necessary to the "measurement" of *R*, then what *R* measures is certainly not a sensation; for nobody will pretend that a straight line is a constituent of a sensation of hue. The line would be necessary, if it turned out either that observers refused to assign numerals directly instead of indirectly by means of the line, or that the numerals assigned directly differed systematically from those assigned indirectly.

It seems almost certain that the value of R assigned to a hue depends on the group of hues with which it is associated as well as on the hue itself. If the same hue X were presented, first, with a group all less saturated than X and, second, with a group all more saturated than X, surely the R assigned to X would tend systematically to be greater in the first case than in the second. If so, R (if it is concerned with sensations at all) measures some compound of a particular sensation and of a group of sensations.

Again, it is probable that R depends on the order of presentation, either in time or space. If a group of hues, containing a pair X and Y, so similar as to be just distinguishable, were presented in random sequence, it would sometimes happen that the values of R assigned were in the wrong order. But if X and Y were always presented in immediate juxtaposition, such a mistake would be made much less often. If so, R measures a compound of a sensation and of the order of presentation of a group of sensations.

Lastly, it is remarkable that Dr Richardson combines the values assigned by many different observers who differ systematically. Here psychological questions are involved. But if, as seems at least plausible, a sensation is something characteristic of a single individual, this procedure is not justifiable, unless some criterion is laid down to determine when the sensations of two individuals are the same or are equal. One conceivable criterion is that individuals exposed to the same stimulus experience the same sensation; this criterion might justify Dr Richardson's practice of taking the mean of the R's assigned by different observers; but it is inconsistent with his deliberate statement that observers differ in their sensations of the same stimulus. Another conceivable criterion is that observers experience the same sensation when they react in the same way. But then the systematic difference between observers shows that there can be no law between R and S; for R is the reaction, and different S's are undoubtedly associated with the same R. I can discover no criterion that is not either utterly unreasonable or inconsistent with Dr Richardson's practice.

§ 9. FINAL CONCLUSION

To sum up, there is no reason to believe that R, if it measures anything, measures a sensation, and much reason to believe that it does not. Again, if it measures something, that something is not certainly different from the stimulus S, and is certainly something that is measured more satisfactorily by an indirect process, involving S, and not by the direct process of guessing. The only apparent objection to measuring this something by means of S is that it then becomes impossible to state a numerical law between S and R. But, since there is no evidence that the law that Dr Richardson proposes is true and not merely empirical, this objection has no weight.

In fact, I think the position can be summed up by another analogy, which I hope will not be thought too frivolous. I know a street in which the houses are numbered and graduate definitely from fine houses with large gardens at one end to something like slums at the other. I believe that the citizens of the town in which it lies could be induced (even in these days) to represent the social position of the occupants of those houses by points on a line, and thus to assign values of R to them, according to Dr Richardson's plan. If so, the R values of the occupants plotted against the numbers of the houses would give a definite curve. But, in my submission, that does not prove that the numbering of houses is measurement or that the problem of measuring social position independently of wealth has been solved. The most that it proves is that the conventional estimate of social position is influenced largely by the character of the house occupied.

§ 10. MEASUREMENT BY ORDERING DIFFERENCES

One last word. I may seem to have proved too much. Surely, an objector may say, there is some significance in the fact that observers agree so well in their "mental estimates." Certainly; it may be a very interesting psychological fact; but Dr Richardson has not produced any evidence that it is significant in the problem of measuring sensations. Again, he may say, surely there must be some meaning in the fact that the curve relating S and R is not a straight line, but has definitely some other form. This objection requires rather more attention.

The curvature of the (S, R) line arises from our power of ordering, not only hues, but also differences between hues. Almost everyone will agree, not only that a buttercup is yellower than milk and milk than snow, but also that the difference between a buttercup and milk is greater than the difference between milk and snow. Now it can easily be shown that if we could order in this way all the differences between sensations, that is to say not only first differences, but also second differences, third differences, and so on indefinitely, then a process of measurement would be possible by means of which we could assign numerals quite uniquely. (Perhaps I had better explain, for the benefit of the possible psychologist reader, that second differences are differences of first differences and so on.) A simple example will show what I mean. If we have 5 hues, A, B, C, D, E, and a choice of the numerals 0 to 10 to assign to them, and if we know that the hues stand in that order, then we can assign the numerals in many ways, so that the order of the numerals agrees with the order of the hues. But if we know also that the differences between the hues stand in the order A–B, B–C, C–D, D–E, then we have only one choice; the assignment must be A 10, B 6, C 3, D 1, E 0. If we knew the order of the second differences, the choice would be uniquely determined, even if we had more numerals at our disposal. Here is a system of measurement theoretically possible; the algebra of it is simple, but need not be elaborated. For as a matter of fact, we can rarely, if ever, order any differences higher than the first or second. Dr Richardson's curve is merely an indication that, in this case as in many others, we can order first differences; it provides no evidence that we can order any of the higher differences that must be ordered if measurement by guessing is not to be inferior to substitutes already available.

DISCUSSION

Dr R. T. Beatty. As a physicist I agree with Dr Campbell's view that physical measurements are most accurately performed by methods of coincidences or of equality of sensations. But such methods cannot be employed to compare, numerically, sensations of different magnitude: such comparisons are apparently intuitive; their accuracy can neither be confirmed nor disproved by any other individual, and as a rule the individual who makes them is unable to indicate the factors on which he bases his numerical comparison.

Many people are able to compare the loudness of sounds. Experiments carried out by Ham and Parkinson* with 175 observers showed that with two pure tones of the same frequency an intensity ratio of 8 to 1 corresponded to a loudness ratio of 2 to 1, and this relation held good over a large range of intensity. Similar results were obtained by Richardson and Ross† though the scatter in their experiments was considerable. In the domain of vision I have made experiments on 50 observers. With the eyes in a definite state of light-adaptation, two lights of the same colour were flashed in rapid succession on a screen, the duration of each flash being one second, and comparisons were made of subjective brightness. When the illumination ratio was 8 to 1 the subjective brightness-ratio was on the average adjudged to be 2 to 1.

This agreement may appear to be merely a coincidence. But in view of what physiologists tell us about the similarity of response of sensory nerves, whether excited directly or by means of a stimulus applied to their end-organs, we may suspect a relationship.

A most interesting result has been obtained by Adrian‡, who measured the number of nerve impulses produced per second when the optic nerve of a vertebrate was stimulated by light falling on the retina. Under steady illumination adaptation occurred and the frequency of the impulses decreased, but if we consider only the initial outburst of impulses we find from Adrian's curves that when the intensity-ratio of illumination is 8 to 1 the corresponding numbers per second of nerve impulses are in the ratio of 2 to 1.

From these results one may be justified in stating the following hypothesis. When two sensations of loudness or of subjective brightness are mentally compared as a numerical ratio, the ratio is based on, and its value is comparable with, the ratio of the frequencies of the nerve impulses which evoke the sensation.

How is the numerical ratio transferred from nerve to mind? I suggest that it is by experience of muscular sensations. The relation between weight lifted and number per second of afferent nerve impulses from the muscles concerned is one of simple proportion, unlike the relation found by Adrian in the case of vision. A muscle is composed of individual fibres, each of which is either relaxed or completely contracted. If 10 fibres must contract when a 1-lb. weight is lifted, 20 are required for 2 lb., with a corresponding doubling of the number of nerve impulses per second. The sensations evoked are correlated with the knowledge that in one case one object is lifted, while in the other case two similar objects are lifted, and so a numerical ratio is assigned to the magnitudes of the sensations, a ratio which is identical with the ratio of the frequencies of the nerve impulses.

---

* *J. Acoust. Soc. Amer.* **4**, 511 (1932).

† *J. Gen. Psychol.* **3**, 288 (1930).

‡ *J. Physiol.* **63**, 378 (1927).

If we assume that this interpretation of sensory messages is transferred more or less accurately to the domains of hearing and vision, we have an explanation of the experimental results already mentioned.

Mr R. J. BARTLETT. From one point of view measurement is a scale reading—the distance from a datum. In measurement a scale is presupposed. Now a scale of orangeness might be prepared by continued division of the distance between yellow and red by the method of equal-appearing intervals. A scale of the same number of points could be prepared by the quantitative mixing of red and yellow as on the colour wheel. If the various points on the one scale are approximately identical with those on the other, it would be reasonable to accept the physically determined scale rather than the psychologically determined scale as the more accurate. If, however, there is a marked difference between the two, the psychologically determined scale must be accepted as the more correct scale of orangeness, and interest will centre in discovering, if possible, a law that will connect the two scales and so enable the more consistent physically-determined scale to be converted into a scale that is psychologically true.

Mr J. GUILD. Dr Campbell's paper deals with a subject which, at first sight, does not appear to offer much interest to physicists as a whole. Direct interest in these problems among physicists is probably confined to those who work in branches of optics and acoustics in which there is some overlap between physics, physiology and psychology. Nevertheless, discussion of the specific question on which Dr Campbell and Dr Richardson are at variance raises wider issues which ought to be of interest to every member of this Society.

Dr Campbell is the author of the only text-book which has been written on the theory of measurement, so I presume we may take it for granted that every physicist is familiar with his views. Needless to say, on so vast a subject there are minor points on which differences of opinion can arise, and unfortunately one is involved in the present paper. Dr Campbell puts forward the thesis that two methods of experiment measure the same thing if the numerals obtained by them are always in the same order. In my opinion this criterion, while necessary, is not sufficient. Further criteria are necessary, which, though expressible in various ways, originate in the theory of similar relations. I do not, however, wish to discuss this question further and thereby divert attention from the author's main conclusion, which is that whatever the experiments of Dr Richardson and Mr Maxwell actually accomplish they certainly do not "measure sensation."

I am in complete agreement with this conclusion, which necessarily emerges from any method of analysing these experiments, and follows from the fact that there is not a one-one relation between stimulus and sensation.

The entities which enter into these experiments are not identified except by reference to specified stimuli. The observer is presented with three stimuli, S_1, S_2 and S_3 and finds a certain order to exist among entities which have to be described as "the sensation evoked by S_1," "the sensation evoked by S_2," and so on. These entities belong to the class of things called *descriptive functions* and cannot be identified with any one of the terms occurring in them. The *R*s with which the observer experiments are not, therefore, either sensations or stimuli: they are complex functions involving both.

If the relations involved in these functions were known to be one-one (not merely not known to be not one-one) we should be entitled to regard each function as serving to identify a sensation. This would still be insufficient to constitute a method of measuring these functions a method of measuring the corresponding sensations; but we need not discuss this latter point because, as a matter of fact, we know quite well that the relation between stimulus and sensation is not one-one but varies with every alteration in the conditions.

In order to obtain a one-one correspondence it is necessary to extend each descriptive function by inserting an instant of time, obtaining "the sensation evoked by S at the instant t." The relation "evoked by S at the instant t" is one-one between stimulus and sensation and serves to identify a sensation in the same limited sense that "the word being spoken by Dr Richardson at the instant t" serves to identify a particular word even if we have no knowledge of what word it is.

But it is clear that we cannot interpret the *R*s which emerge from these experiments as definite descriptive functions of this kind, for immediately we make them definite by specifying instants we also make them ephemeral. Their significance is confined to the specified instants and cannot be maintained throughout a system of relations involving several experiments. Any law emerging from a series of experiments cannot concern the definite functions involving instants, but must subsist between the ambiguous functions which do not involve instants, and which, for that very reason, cannot serve to identify sensations.

The preservation of the identity of the function "the sensation evoked by S_1," say, throughout a series of experiments, does not involve preservation of the identity of any sensation. Now it is essential to the meaning of a relation that all the terms which appear in it shall preserve their identity throughout the whole series of operations involved in determining the relation, and, as this is not true of sensation in experiments in which sensations are only indicated by reference to stimuli, any relations obtained cannot be relations subsisting among sensations.

The sensations evoked by the two terminal stimuli to which the observer relates the intermediate member are not, as Mr Maxwell claimed in his remarks, standards of sensation, but are standards of the complex function "the sensation evoked by S"; and the R to which the results apply does not denote the one term, sensation, but denotes the entire function.

It is impossible here to discuss the distinction between a descriptive function and the terms which appear in it, but a consequence of the distinction is that things which are true of the function are not necessarily true, or even significant, when said of any individual term, and *vice versa*. The function and its terms are entities of different mathematical types, and to confuse "the sensation evoked by S" with a definite individual sensation is a gross error in logic.

There is a plentiful field of experiment for psycho-physicists in determining the relations between ambiguous descriptive functions of this type, but a clear appreciation of their meaning is necessary if the interpretation of the results is not to remain permanently obscure.

It will always remain obscure so long as a relation such as that shown by Mr Maxwell's curve is assumed to be a relation in which the related terms are sensations and stimuli. It is a relation in which each value of the independent variable is a stimulus, and the corresponding value of the dependent variable is that member of the class of ambiguous descriptive functions "the sensation evoked by S" which is obtained by putting the stimulus in question for S. Each sample of the dependent variable itself involves an *undetermined* relation between stimulus and sensation.

All this follows from the nature of the experiment and does not depend on what the observer *thinks* he is doing when he assigns values to the dependent variable. In order to get any further in the process of interpretation, we must consider to what extent the results represent a subjective interpolation of the phenomena *actually existing during the experiments*, and to what extent they are influenced by past experience of the appearances presented by combinations of stimuli.

It would be very difficult for an experienced photometrist or colorimetrist to perform these experiments "honestly." Despite himself his judgment would be influenced by knowledge of the stimulus combinations required to produce appearances similar to those presented to him, and the "values" which he assessed would be little else than estimates of the stimulus ratios. This process is truly, as Campbell suggests, only an attempt to measure stimulus ratios by a rather unsatisfactory method. There are very few members of the community who have not picked up ideas—none the less definite because they are frequently wrong—on the association of appearances with stimulus characteristics. The influence of these ideas on the observer's "answer" cannot be eliminated just by instructing him not to think about them. They would have to be eliminated not only from his conscious intentions but from the records which exist in the neurones of his central nervous system.

In my experience the preconceived ideas of the man-in-the-street on colour-mixing, for example, are not less definite than those of the experienced colorimetrist. They differ from his only in being less nearly in accordance with physical facts. It is possible, therefore, that an inexperienced observer when performing an experiment of this kind is doing exactly the same thing as a colorimetrist would almost certainly be doing; that is, guessing the stimulus ratios, the only difference being that his guesses would have a greater tendency to be systematically wrong owing to the wrongness of his preconceived notions.

I do not see that we can definitely conclude, without further evidence than is contained in the experiments themselves, that the departure from a straight line exhibited by Mr Maxwell's results indicates anything more than a systematic wrongness in preconceived ideas on additive colour-mixture, based, as are most people's ideas on colour-mixture, on a miscellaneous experience in which subtractive colour-mixing predominates.

I do not suggest that this is all that is involved in the curve, but merely that it is by no means proved that anything else is involved. If it could be shown that similar results were obtained by observers so entirely ignorant of the world they live in as to have no preconceived ideas on anything, we could then definitely conclude that a true subjective ordering of immediately present sensory phenomena was involved; but persons of this kind are hard to find, even among psycho-physicists, and some doubt must, apparently, always remain regarding the extent to which judgment based on memory enters into such experiments.

In conclusion I would refer to a more general matter. Whenever discussions of this kind arise concerning the meanings of words and processes there are always some who regard such discussion as mere "hair-splitting" and quibbling over unessential distinctions. "Let us get on with our experiments," they say; "what does it matter whether we call a process *measurement* or not, or whether we call the things with which we experiment *sensations*, or ambiguous descriptive functions, or anything else; it is the results that matter." This attitude, in my opinion, reaches the limit of absurdity. It is tantamount to the assertion that it doesn't in the least matter that we should know what we are talking about. Results cannot "matter" until we express them in propositions of known meaning. If I assert that I kick a football, this only becomes intelligible because *kick* denotes a certain process and *football* denotes a certain kind of object. If I make an assertion in these words and then qualify it by saying that it doesn't matter whether kick means the process which this word usually denotes or football the kind of object which this word usually denotes, what fact have I succeeded in describing?

The significance of any asserted fact does not lie in the mere sound or grammatical form of the assertion but in the meanings of the words used and the kind of relations in which these meanings stand to one another.

If we wish to talk about measurement in connexion with sensations, then measurement must *mean* measurement, and sensations must *mean* sensations—the things actually *felt*—and not entities of a different mathematical and logical type. Any statements involving these words but not these meanings can never be anything but sheer nonsense.

Dr W. D. WRIGHT. I hope our ideas on visual sensations will be clarified as a result of this discussion. I was, however, disappointed with the oral remarks of Mr Guild, in whose opinion I have considerable faith. I am afraid I followed very little of his argument, but I did gather that he looked on the measurement of visual sensations as a particular example of some general proposition. This method of attack is usually to the disadvantage of the particular problem. Hence my disappointment. This was the more unexpected as Mr Guild had already dealt clearly with the problem in his discussion of Dr Richardson's original paper. If I may quote, he says there "But we cannot *measure* the magnitude of a sensation. We cannot experimentally isolate a unit of sensation from which to build up a quantitative scale of magnitude as required by all processes of measurement. This does not mean that we cannot make subjective estimates of the magnitude of a sensation: that in fact is the only means we have of obtaining quantitative information about sensations." With all of this I am in entire agreement. If now we apply this view, it seems to me that the outstanding points of Dr Campbell's paper lose their significance.

For example, Dr Campbell concludes that since R varies with S, in all probability R simply measures S in a bad way. But if R is a mental estimate of the magnitude of a sensation, then it certainly is not a measure, good or bad, of S. It must be one or the other, but it cannot be both, and I think Dr Campbell is wrong in regarding it as a measure of S.

Again, Dr Campbell, quite rightly, assumes that R will vary with the simultaneous or successive contrast to which the eye may be subjected. But to suggest that, assuming *R did* measure a sensation, it would in this case measure a compound of sensations, is quite wrong. R is an estimate of a particular sensation, an entity which, certainly, is affected by the experimental conditions but only as regards its magnitude and not its quality. (We must assume that the colour remains on the same line between white and red.) Hence while the magnitude of the sensation is changed, R is still an estimation of this magnitude and not of any compound of sensations. An analogy may make the point clear. If we had a basket containing a dozen apples, 12 would represent the number of apples in the basket. If, now, a boy came along and stole four apples, there would be eight left. Then 8 represents the number of apples now in the basket, but on Dr Campbell's argument 8 measures a complex function of the apples, the basket and the boy.

I am in partial agreement with Dr Campbell in his argument against combining the values from different observers. Evidently if each individual experienced a marked difference in sensation for the same stimulus, such a combination would be meaningless. For instance, a smooth curve between R and S that was obtained by combining results for a number of normal observers and a number of colour-blind observers would be meaningless. The result would correspond to no known individual. But for observers who have normal vision the mean curve simply represents what an average observer gives as his estimate, and includes the effect introduced by the minor variations evoked by the same stimulus. It is admittedly necessary to assume that these variations are relatively small and distributed about a mean, but Dr Campbell apparently considers that they must be non-existent.

One last point. It appears to me that Dr Campbell's suggested method of measuring sensations by ordering differences is, in effect, the same process as that implied in the Weber-Fechner law, namely the ordering of sensations by observing just-noticeable differences of sensation for varying stimulus. The novelty of the method is therefore doubtful. In any case, as Mr Guild has indicated, we cannot measure sensations, and this method, with any others, must be discarded.

Mr T. Smith. An essential question involved in this discussion is the meaning, and possibly the need for limitation of the scientific use, of the word "measurement." I should like to express my agreement with the position Dr Campbell has taken up in his book *Measurement and Calculation*, and the view that Dr Richardson's application of the word to mental estimates is unfortunate and inconvenient. The arguments used in this paper must be read in conjunction with the more detailed discussion in Dr Campbell's book, for owing to the need for brevity some conditions essential for the validity of the arguments are not specifically referred to, e.g. the limitation to a closed set of the numbers used to express measurements.

Measurements other than those of derived magnitudes depend upon a procedure by which two magnitudes A and B can be conjoined so as to be equivalent in some respect to a third magnitude C belonging to the same group as A and B. Provided this relation obeys some well-known conditions the process can be assimilated to arithmetical addition, and hence numerical values can be assigned which enable connections to be established with numbers corresponding to other measurable properties. If it were possible to devise a process for synthetizing two sensations so that in some respect they were jointly equivalent to a third sensation we should be able to measure sensations. In the absence of such a process careful examination shows that, whenever real measurement is carried out, it is not a sensation, whatever else it may be, that is being measured.

In investigating estimates of the ratios of sensations Dr Richardson is examining a matter of very general interest, but I suggest that part of his procedure is open to criticism. It may be that some people readily and naturally form definite judgments of the relative intensities of their sensations, but many of us find the process artificial and very uncertain. Sensations sufficiently akin can be placed readily enough in a definite order, an order in which general agreement can be obtained. If, for this discussion, we use the symbols $\leqslant$ and $\geqslant$ to denote "slightly less than" and "slightly greater than" with respect to some property for which less and greater have been defined, the useful relations between sensations of the same class can to my mind be adequately described by the series of symbols

$$<<, <, \leqslant, =, \geqslant, >, >>.$$

The only point on which I am uncertain is whether it is not also desirable to add $\sim$ to express the relation between those sensations for which we find it difficult to decide between $\leqslant, =, \geqslant$ owing to the unavoidable intrusion into our consciousness of other properties than the one under consideration. If I may take an example from Dr Richardson's recent paper "A quantitative view of pain"* in place of his scale $A = 3$, $B = 20$, $C' = 30$, $C = 70$, $\alpha = 100$, $D = 200$, $E = 500$, $\beta = 500$ (C' represents C when the sufferer's attention was distracted from his pain), I should probably not be able to say more than

$$A < < B \leqslant C' < C \leqslant \alpha < D < E = \beta.$$

We hear children make such remarks as that one kind of pain is "ten times worse" than another, but I have always regarded this as a child's way of saying "much worse." To Dr Richardson the numbers apparently have a meaning, but to me the statement that a certain pain is ten times as intense as the one I am experiencing carries no precise significance. The conjunction of numbers and sensations may sometimes be merely a matter of mental association, comparable for example with the association formed by some people of the days of the week with particular colours. If I understand Dr Richardson correctly he claims to recognize ratios in sensations, but not to be able to recognize the intensity level of a single sensation. For example, in the paper referred to the scale is defined by taking α as 100, where α is "that pain which just prevents one from going to sleep at the time and under the circumstances in which one does ordinarily fall asleep when free from pain." A definition of this kind is not without its dangers: to take a somewhat analogous case concerning the sense of hearing, one may ordinarily not be awakened by a violent thunderstorm at the time and under the circumstances in which one is ordinarily awakened if one's name is spoken.

---

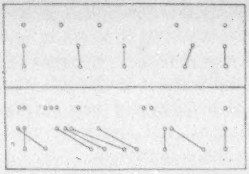
* *Brit. J. of Psychol.* (General Section), **23**, 401–3 (1933).

Mr Maxwell and Mr Bartlett appear to be concerned with the comparison of intervals or differences between sensations rather than ratios. Mr Maxwell refers to interpolation between standard sensations; but the sensations in fact are not standards, but merely the sensations resulting at the particular time from exposure to standard stimuli. Apparently Mr Maxwell does not rely on judgments of ratios of intensities, though for Dr Richardson these "ratios were estimated in a manner so direct as to elude analysis." If I may judge from my own trials and those of some of my colleagues who have made colour experiments on the lines proposed by Dr Richardson, the estimation of these ratios is commonly difficult and the process is both slow and indirect. Even though efforts were made to disregard any knowledge based on general experience of measurements, the results suggest that the numbers obtained were influenced by past experience where this existed. In general there are wide differences* from one person to another in the values reached as well as in the mental paths followed in obtaining them. I can therefore neither subscribe to the implications of Mr Maxwell's claim that the observer "knows his own mind" nor on the other hand attach importance to Mr Maxwell's mean curve, which is assumed to be a function solely of the form of the question and the answer given, and independent of the varying criteria adopted by different subjects.

My own trials lead me to think that in some of these investigations the number of arbitrarily fixed points is too small to define a scale. For example, in placing a pink on a scale bounded by white at one end and red at the other I may try to imagine the appearance of a coloured band which changes "uniformly" from white to red, and to place the pink strip at the appropriate position of the band. I then encounter the difficulty that "uniform" is so uncertainly presented to my imagination that a pink physically half-way between the white and the red may occupy any position in the central half of the linear interval, and may conceivably even lie outside it. If any position within this large fraction of the whole length is selected, there is no difficulty in placing additional colours of the white-red series with considerable precision to form what appears to the eye as a "uniformly" changing series. This experience may imply that the particular intervals white to pink and pink to red are dissimilar in type, so that there is no intrinsic meaning in their ratio: it suggests on the other hand that compound ratios invariant on projection may be of significance. The process is certainly very different from that involved in comparing two lengths.

---

* As far as I can judge the spread of the observed points in my experiments was distinctly greater than in those of Mr Maxwell. This appears to me to be largely a matter of chance; the spread is not necessarily of importance.



The accompanying diagrams may be of interest. The isolated points of the top row in the upper diagram represent the positions assigned to colours by Richardson's method, the colours varying from red through yellow to yellowish green. The corresponding row of points in the lower diagram relates to a blue-green series of low luminosity. The bottom row of each diagram represents measurements of the stimuli. Three suitable members, representing approximately the extreme and the mean of the top scales, were used to determine a projection so that the positions of the three estimated points were moved to coincidence with the corresponding measured points. The projected points are shown on the middle line, and connections between measured and estimated points are added. In the upper diagram the two additional joins are approximately vertical, and suggest that the estimates are projectively related to the stimulus measurements*. The approximate parallelism of most of the joins in the lower diagram suggests that a similar relation holds here also, the points which happen to have been chosen for reference being the least regular. The irregularities, including the one reversal of order between measurement and estimate, are undoubtedly due to the disturbing effect of differences in luminosity, though these differences were not really great. These two examples certainly do not contradict Dr Campbell's conclusion that, however unconsciously, our numerical estimates relate to the stimulus. I ought to add that I have no experience of colorimetric measurements, so that the distribution of my points was not in any way influenced by a knowledge of what measurement would yield.

Dr J. H. Shaxby. I am in general agreement with the views of Dr Campbell on these problems of sensory magnitudes. I confess that I have never been able to persuade myself that such an estimate as this of a pink, by placing a point on a line whose extremities represent red and white, is not an assessment of stimuli rather than of sensations. If I try to estimate a weight in the same way in relation to two other weights, one lighter and the other heavier, I seem to be asking myself what weight will produce the same sensation by interpolation between the sensations given by the two extreme weights, i.e. I am making a judgment of stimuli.

---

* It is pertinent to remark that different systems of colour scales are projectively related to one another.

The particular stimulus in question in the red-pink-white test is not so obvious as in the matter of weights, but I cannot feel that there is any essential difference between the two cases.

In other words, I seem to be using my sensations as a sort of apparatus to form a scale of measurement of the stimuli producing those sensations. If I knew nothing of the experimental work on just-perceptible-differences, I should be tempted to call this scale a linear one, that is to associate equal lengths on it with equal changes in the stimuli. That this is not so seems only to indicate that my sensory apparatus gives "readings" related to the stimuli in a way more complicated than that of proportionality, and not to justify me in supposing that I am measuring something quite different, namely my sensations. I am no more establishing a scale of sensations than, in using the positions of the deflected pointer of a galvanometer, I establish a scale of angular measurement. Just as I assume this scale of degrees in using the galvanometer, so I assume a sensation scale as the indicator of gravitational or pinkness stimuli, and in the very act of doing this I rule out any possibility of finding out anything fundamental about the quantitative aspects of sensation. I have consciously or unconsciously made a definite, but unverifiable, assumption about my sensations, and, having done so, I may not argue back again to any law of magnitude of sensations.

In all such tests we use our memory of previous (even if immediately previous) sensations to make the very sort of test that Dr Campbell shows that we can make more sensitively by an actual variation of stimuli to produce a sensation not differing appreciably from the one experienced: a sort of null method.

Further there is the great difficulty of adaptation, which affects all our sensory estimates. Such methods as these under discussion not only leave the degree of adaptation out of account, but necessarily make its value indeterminate.

Incidentally, what sensations or stimuli are estimated in Dr Richardson's experiments? In the simplest way of conducting them one end of a line stands for maximum redness, the other for maximum whiteness, but also there is least brightness at the red end and greatest at the other. Are we then judging by redness, whiteness, redness versus whiteness (saturation), brightness, or a combination of these? It must surely be some combination, for if we made the brightnesses of the red and of the white (grey) each equal to that of the given pink, we should, I think, get a different position of the pink on the line. In other words, in marking a point on the red-white line we are attributing to a unique sensation a particular position on a scale, but this scale is not a function of any simple sensation or stimulus, and we have no means of knowing the parts played by different variables in fixing the scale.

Major J. L. P. MACNAIR. I think the controversy really goes a good deal deeper than any question of stimuli or sensations. Briefly it appears to me to resolve itself into the fundamental problem, about which psychologists are still by no means agreed—have we a mind or not? If we have, R might represent some form of subjective measurement. If not, and all perception is purely physiological, then S is really the same thing as R, though there may be many intermediate steps.

But even in the latter case, to measure anything physically we must have something to measure it against. What? I do not find Richardson's analogy of the $\frac{1}{10}$-centimetre guess convincing. When judging $\frac{1}{10}$ centimetre we are in reality making a mental comparison with a measuring rod whose form is very familiar to us.

Mental measurements, if really distinct from physical comparisons, must be absolute. But what is absolute mentally always turns out to be relative when looked at physically; see Dr Thouless's experiments on the projectional visual observation of an inclined ellipse. It is practically impossible to say at what stage an ellipse rotated about its minor axis projects a circle to the eyes, because the mental process takes into account the surrounding objects. Hence the very seeming inaccuracies complained of by Dr Campbell are in a way a support for mental theories. For this reason also orders of difference cannot, I think, possibly provide a method of approach.

The difficulty will not be finally resolved until we have decided whether mind is to be regarded as separate from body or not. At the same time the "philosopher in the street" (whom I diffidently claim to represent) must welcome Dr Campbell's interesting and provocative paper and the discussion it has aroused, as helping us towards such a decision.

Capt. C. W. HUME. Whenever by inadvertence I get into a hot bath with cold feet I always look at the thermometer. In the trying circumstances it is a great comfort to reflect that this latter is an instrument of precision whereas my mental estimate of the intensity of sensation is fallible if not meaningless. I just take the logarithm of the absolute temperature, and bear in mind that this is the only quantity that has assignable significance.

Dr J. O. IRWIN. I have been struck by the fact that there appears to be an analogy between a judgment of sensation and a judgment of probability. Probability is defined by Mr Keynes as the degree of rational belief in a proposition on certain evidence. Strictly speaking for given evidence there can only be one rational degree of belief in a proposition, but Mr Keynes admits that different people might differ in their degree of belief in a proposition on the same evidence. He says, for instance, "Some part of knowledge, knowledge of our own existence or of our own sensation, is clearly relative to individual experience. We cannot speak of knowledge absolutely —only of the knowledge of a particular person. Other parts of knowledge—knowledge of the axioms of logic, for example, may seem more objective. But we must admit, I think, that this too is relative to the constitution of the human mind and that the constitution of the human mind may vary in some degree from man to man. What is self-evident to me and what I really know, may only be a probable belief to you or may form no part of your rational beliefs at all. And this may be true, not only of such things as *my* existence but of some logical axioms also....What we know, and what probability we can attribute to our rational beliefs, is therefore subjective in the sense of being relative to the individual. But given the body of premises which our subjective powers and circumstances supply to us, and given the kinds of logical relations upon which arguments can be based and which we have the capacity to perceive, the conclusions which it is rational for us to draw stand to these premises in an objective and wholly logical relation."

For "degree of rational belief in a proposition on certain evidence" substitute "sensation evoked by a stimulus under certain conditions" and the analogy begins to appear. If we could make the conditions sufficiently precise it is difficult to believe that we should not get a unique sensation corresponding to a given stimulus, but in actual practice different people may differ in the sensation evoked by a given stimulus, or the same person may differ on different occasions.

It does not follow that the sensation is measurable any more than it follows that the probability is measurable. One may again quote Mr Keynes. "There are some pairs of probabilities between the members of which *no* comparison of magnitude is possible; that we can say, nevertheless, of some pairs of relations of probability that the one is greater and the other less, although it is not possible to measure the difference between them; and that in a very special type of case, to be dealt with later, a meaning can be given to a numerical comparison of magnitude." For "probability" substitute "sensation," and would anyone seriously quarrel with the statement? We may note in passing that of course probability in the sense of "degree of belief" is quite a different thing from "empirical frequency" or the relative number of times an event will happen in the long run, but again under some circumstances there will be an intimate connexion between the two.

The following extension of the analogy is perhaps no more than suggestive. If we write R for stimulus and dS for a small increment of sensation we might write

$$dS = f(R)\, dR,$$

meaning that the just perceptible difference in stimulus is some function of the stimulus increment*. Now dS, as Dr Campbell has shown us, does not measure sensation, but it may be related to it. Now suppose we are examining some measurement—say the stature of a few hundred or thousand individuals—let us write x for stature and dx for a small increment of stature: then we shall find $dp = \phi(x)\, dx$, where dp is the proportion of individuals whose stature lies between x and $x + dx$. Now dp is not a probability, it is an empirical frequency; but it is closely related to a probability. Is it too fanciful to suppose that dS is related to sensation as dp is related to probability? To complete the analogy we should have to be able to identify dp with the smallest difference in stature (x) such that for the two values x_1 and x_2 between which the difference lies one of the two propositions "the stature of this man is x_1" and "the stature of this man is x_2" could be judged more probable than the other. Is this legitimate? At any rate it raises the hope that some competent logician might be able to state precisely the conditions under which sensation would be a measurable quantity.

Again I can see no reason why keen experimentalists should not ask people to make mental estimates or guesses of the point on a line which corresponds to the probability of a given proposition on given evidence, just as Dr Richardson has obtained mental estimates of colour-saturation, loudness and pain.

---

* If $f(R) = c/R$ we have Weber's law.

The Rev. R. S. MAXWELL. In his analogy with temperature in paragraphs 2 to 5 Dr Campbell appears to have begged the question with regard to the experiments conducted by Dr Richardson and myself. Throughout, we were concerned with the measurement of sensations, not of stimuli. The sensation of warmth is surely a different thing from temperature. It may be granted that any such measurement is in a very primitive stage and is not necessarily very accurate. The underlying question appears to be "Is it possible to make any such measurement quantitatively at all? I.e., can we assign any numerical value to such sensations as we may experience in terms of standard sensations—a standard sensation being defined as the sensation produced by a standard stimulus?"

I should be prepared to maintain that the answer to such a question is definitely in the affirmative. I have tried it myself in the case of colour estimations*, the loudness of sounds in a telephone receiver†, and the temperature-differences of water in various beakers. I feel that for myself I can assign a definite numerical value to such sensations. Call it guessing, if you will. No one would expect a very high degree of accuracy in the use of such a method, but I feel that what I measure is an internal sensation, and not an external stimulus.

Take the question of temperature-differences in more detail, since Dr Campbell refers to it especially. A few days ago I tried the following experiment. I took two beakers containing water at 25° and 35° C. respectively, and got an assistant to pour water of an unknown temperature into a third beaker. I placed the first finger of the right and left hands into the hot and cold water respectively. This gave me a standard sensation produced by a standard temperature-difference. After fifteen seconds I transferred the right hand into the beaker containing the water at the unknown temperature. This gave me the sensation due to an unknown temperature-difference, and I felt quite confident in assigning a numerical value to such a sensation, and although I should not be prepared to claim any high degree of accuracy for it, I definitely feel that it did represent a quantitative mental estimate of temperature-difference. When fourteen such estimates were made, the results, although somewhat scattered as might be expected for such a crude experiment, did lie more or less evenly distributed about a straight line.

One final suggestion. Is it possible that the whole controversy has arisen through a misunderstanding of the meaning of the words used by Dr Richardson and Dr Campbell? The quantitative mental estimates either of colour, or sound-intensity, or temperature-difference made by Dr Richardson and others do appear to have some perfectly definite meaning even if they do not conform to Dr Campbell's more rigorous definition of the word "measurement." Would it not be possible to use the word "estimate" rather than "measurement" in such cases? Dr Richardson himself appears to hint at some such course when he suggests that "Sensation belongs to some more primitive type of magnitude which has hitherto escaped classification"*.

---

* R. S. Maxwell, *Brit. J. Psychol.* **20**, 181–9 (1929).

† L. F. Richardson and J. S. Ross, *J. of General Psychol.* **3**, 299–300 (1930).

Dr R. A. HOUSTOUN. It would help to clarify our ideas if Dr Campbell could answer the following questions on the subject of his paper. The visible stars have been divided into six magnitudes since the time of Ptolemy. For centuries the estimation was made visually, but now it can be done photometrically by comparing a star with the pole star or with an artificial star and altering its intensity by means of a nicol prism, or it can be done photographically by measuring the blackening of the image. The results obtained by the three methods can be related by formulae.

What did Ptolemy measure by his magnitudes, if it was not sensation? Is the term "measurement" to be withheld from the results obtained by the visual method and allowed to the results obtained by the other two methods?

Reply by Dr L. F. RICHARDSON:

1. Physicists are accustomed to estimate mentally, or if you prefer to guess, tenths of a scale division; also to guess tenths of a second when using a clock beating whole seconds. But let no one suppose that I advocate an extension of guessing in practical physics; for I really admire the growth of instrumental precision. The present controversy is not about physics but is about logic, psychology and metaphysics.

2. If anyone desires to read the theory of order and quantity set out with clarity and charm let me recommend *The Fundamental Concepts of Algebra and Geometry* by John Wesley Young†. Of course we must all agree with Dr Campbell that "a process of assigning numerals is not regarded as measurement unless it fulfils conditions more stringent than the mere representation of order." But mental estimation gives more than mere order. This is well known in connexion with estimating tenths of a scale-division. Again, if you saw an ordinary street of houses all alike numbered consecutively 1, 2, 3, 14, 25, 638, 639, would you not feel that although the order was correct the numbering was silly? Would you not feel this immediately without needing to measure distances with a tape? If so you become immediately aware of more than mere order. Dr Campbell admits this himself in regard to yellowness in his § 10 and indeed he proposes an ingenious difference-method for assigning numerals.

The serious question is not whether sensory events are quantitative, but how accurately they are quantitative. That can be found out by psychophysical experiment, but never by mere argument. Here follows a suggestion for a crucial experiment. Let four stimuli A, B, C, D, steadily increasing from A to D in some quality, be adjusted so that the successive intervals of sensation appear equal when the stimuli are considered in adjacent pairs, namely AB with BC and then BC with CD. How nearly does the interval of sensation from B to D then appear to be twice the interval of sensation from A to B? The accuracy of this result is known to be good when the sensation is that of lengths drawn on paper, but for loudness, colour, warmth, taste and pain there is I believe as yet very little definite information about accuracy in this sense, although there is already a good deal of information about accuracy of repetition of estimates of various sensations.

---

* L. F. Richardson, *Report on Vision*, pp. 112–14 (Physical Society, 1932).

† Macmillan, New York (1911).

3. I disown the remarks of the fictitious Dr Richardson introduced by Dr Campbell in his § 3, and give instead my own conviction that the sensation of warmth is quite distinct from thermodynamic temperature. Similarly for colour. What should we think of a fictitious person who could not distinguish qualitatively between a wave-length and the sensation of colour which it produces?

4. Important in Dr Campbell's argument is his doctrine about the sameness of things. He uses the phrase "the same thing" at least ten times, and in a very peculiar and confusing sense. Thus in § 5 he states that "two methods measure the same thing, if the order of the numerals assigned by one to the members of a group is always the same as the order of the numerals assigned by the other to those same members." Because, as x increases, x^3, $\tan^{-1} x$, $\exp x$ all steadily increase, therefore according to Dr Campbell, x, x^3, $\tan^{-1} x$, $\exp x$ all measure "the same thing." Neither in mathematics nor in common speech is it customary to say that x and x^3 measure the same thing. This doctrine of Dr Campbell's is metaphysical and reminds one of Kant's doctrine of the alleged things-in-themselves behind phenomena. To prevent confusion we ought to have a technical term, and I propose in future to call Dr Campbell's "same thing" a "same N.R.C. thing."

I am now able to state that whereas sensation and stimulus are entirely distinct, yet under specially constant circumstances they are approximately the same N.R.C. thing.

5. A fundamental distinction between sensation and stimulus is that each person has his own immediate experience of sensation, but only an inferred and usually co-operative knowledge of stimuli. Hamlet's epigram on the certainty of immediate experience* may be crudely brought up to date as follows:

Doubt how electrons behave;
  Doubt if anything really is there;
Doubt whether sound is a wave;
  But never doubt you hear,
Unless of course you really *are* not quite certain.

This comic anticlimax supports the thesis, for "not-being-quite-certain" is a personal mental state, very different from a stimulus.

6. The plainest evidence that sensation is not, in ordinary parlance, the same thing as the stimulus external to the human body is afforded by a study of the illusions, Gestalt-phenomena†, eidetic images† and hallucinations. For example a sensation of brightness may be produced either by a train of waves entering the pupil or

---

* Act 2, Scene 2.

† E. R. Jaensch, *Eidetic Imagery* (Kegan Paul, London, 1930); W. Köhler, *Gestalt Psychology* (Bell & Sons, London, 1930).

by digital pressure on the outside of the eyeball. Now if the sensation is the same as each of these different stimuli, it would follow that the stimuli are the same, which is absurd. It may be replied that each kind of sensation is in one-to-one correspondence with a special state of affairs in the brain; but even so, a state of affairs in the brain is not what we mean ordinarily by the "stimulus".

7. With regard to the minor variations in the relation between stimulus and sensation, that is to say setting aside hallucinations and illusions of the more extreme kind and considering only such minor affairs as simultaneous and successive contrast, Dr Campbell gives two strangely different arguments. *Firstly:* when these minor variations are negligible, he regards this in his § 5 as evidence that a mental estimate of a sensation and the measure of a stimulus are the measures of the same N.R.C. thing. I agree, but find the statement rather dull. *Secondly:* when these minor variations are not negligible, Dr Campbell in his § 8 considers that the variations indicate that the mental estimate is not an estimate of a sensation. In other words he accuses the observers of not knowing their own minds. Most people know their own minds more or less, though not perfectly. Dr Campbell condemns the whole procedure because some of the details are unclear. I think it will be much wiser to go patiently on with the experimental elucidation of these variations.

In the last paragraph of his § 8 Dr Campbell attends to the chief difficulty of psychology, namely the privacy of the individual mind. It is indeed a formidable difficulty. Personally I refrain from assuming either of the criteria which he mentions and rejects. It is not convenient to have to remember the individual estimates of hundreds of observers; so I prefer instead to state their mean and their standard deviation. This is a harmless, customary and useful procedure and there is no justification for Dr Campbell's violent condemnatory words.

8. With regard to the functional relation between stimulus and the average of the estimates of sensation, the credit of obtaining the interesting curve, which Dr Campbell attributes to me, is really due to the Rev. R. S. Maxwell, B.Sc.

In discussing this curve Dr Campbell asserts in his § 7 that "Physicists do not regard a law as a true numerical law, unless its form is simple and/or explicable by a theory; if it does not fulfil that condition, it is a mere empirical law." This statement of Dr Campbell's contains, I think, more than one misleading antithesis. For the opposite to "true" is "false," not "empirical." Also the opposite to "simple" is "complicated," not "empirical." For example, Stefan's radiation law was in the year 1880 empirical and simple and true for black bodies, before its thermodynamic theory was published by Boltzmann in 1884. Again, the law by which the tides at any particular port are predicted is fairly true, decidedly complicated and partly empirical. Disagreeing as I do with Dr Campbell's fundamentals on laws, it is useless for me to argue about his deductions on this subject.

9. A restriction of the meaning of the word "measurement" so that it should apply only to what Dr Campbell has named A-magnitudes and B-magnitudes is recommended by several speakers. Such a conventional restriction might suitably be left to the decision of the Committee appointed by Sections A and J of the British

Association in 1932. But I must point out that Dr Campbell formulated his valuable classification of types of magnitude before he had sufficiently considered the existence and properties of mental estimates. Dr Houstoun in this Discussion has mentioned excellent reasons for not thus restricting the meaning of "measurement." Might we not suitably say that mental estimates are "C-magnitudes," and that all magnitudes are measured?

10. Taking each person's word "measurement" in his own sense, I am happy to be in general agreement with the remarks of Mr R. J. Bartlett, Dr W. D. Wright, Capt. Hume, the Rev. R. S. Maxwell and Dr Houstoun and am much interested in the facts brought into comparison by Dr Beatty.

11. As to bias, I agree with Mr Guild that experience of painting, dyeing or of colorimetry would be likely to distort mental estimates of colour. But ordinary adolescents should be much less biased.

12. Mr T. Smith has much to say about the difficulties experienced by himself and some colleagues and mentions by contrast the lesser scatter in the estimates of Mr Maxwell's schoolboys. But the existence of great learning and intelligence in some persons, who find difficulty in making estimates, does not, I think, discredit the estimates of those who make them easily. For among nearly 400 persons, whom I have asked to make estimates, there was no obvious connexion between refusal on the one part and learning and intelligence on the other. Also it is known that various sensory accomplishments are distributed among the population in a manner having no important correlation with general intelligence. According to G. M. Whipple's *Manual of Mental and Physical Tests*[*] this is so for the discrimination of lifted weights and of double touch on the skin. Some very intelligent people are colour-blind, as John Dalton was. An honours B.Sc. is no guarantee that its possessor can sing in tune. Sometimes logical propensities are actually a disqualification. Thus Sir Francis Galton found that imagery was weaker among those accustomed to much abstract thought than among women and children[†]. Again Mr Dudley Heath of the Royal College of Art remarked, in connexion with estimates of pink, that those art-students who decline to make a decision in this and similar problems are those who are also argumentative; and that they could place the mark on the line if they would trust to their first impressions, instead of to reasoning[‡].

Reply by Dr N. R. CAMPBELL:

1. To much of the discussion I can reply generally. I am not competent to discuss whether Dr Richardson's facts are indeed facts, or whether there are similar facts concerning other branches of sensation. In order to limit the issue I do not propose to discuss *here* whether other alleged methods of measuring sensations, e.g. the equal-interval method or the just-perceptible-difference method, are actually measurement. The opinions on these matters are interesting, but beyond my present scope. I am only asking whether Dr Richardson has produced evidence that his method measures sensations, on the assumption that his facts are facts.

---

[*] (Warwick & York, Baltimore).

[†] See W. James, *Principles of Psychology*, **2**, 51–57.

[‡] *Brit. J. Psych.*, General Section, **20**, 36 (1929).

I maintain (in accordance with Mr Guild) that nothing but confusion and error can result from using "measurement" in any but its accepted sense. I call nothing measurement that does not possess the distinctive features of the processes physicists accept as measurement.

I do not deny a difference between sensations and stimuli, and I fully recognize that there are facts, beyond the scope of physics, well worthy of study. But to study is not necessarily to measure. Everything concerned in a process of measurement is not measured by that process—e.g. the colour of a titration indicator or the luminous flux from a galvanometer lamp. To say that two processes measure the same thing is not to deny that there are things, not measured by either of them, in which the processes differ.

2. I will start with Dr Richardson, considering only his main points not covered by paragraph 1.

Estimating tenths is measurement only because it has been shown to agree approximately with better ways of measuring the same thing. In so far as the estimates give a result different from that of the better methods, they are wrong; witness the term "decimal error." And here I may answer Dr Houstoun's question. Until the Ptolemaic method had been shown to agree with physical methods, there was no evidence that it measured anything; it was on a par with Mohs's scale of hardness. Now it has been shown to agree, it is simply a bad way of measuring something that is better measured otherwise. These two examples support, not undermine, my position.

I do not admit that the mathematician's "quantity" is the same as the physicists "quantity." Dr Richardson's citation of Dr Young's work shows well the danger of calling different things by the same name. I do not deny that mental estimates give more than order; but I do deny that they give enough more to constitute measurement. I accept his view that mental estimates are probably an indirect way of recognizing equal intervals; but the question remains whether measurement can be based on such recognition.

I maintain my position about "measuring the same thing", for Dr Richardson's evidence supports it. There are actually no two recognized physical magnitudes related as are x and x^3, or as x and any other mathematical function of x having the same order; $\tan^{-1} x$ has not the same order. The reason is that, when we find ourselves measuring two quantities so related, we realize that they are the same and drop one of them. The nearest approach to the position Dr Richardson contemplates is when we recognize magnitudes (e.g. period and frequency) related as x and $1/x$ or $(1-x)$; but then the order is not the same; it is reversed.

I have not accused observers of not knowing their own minds. A man may know his own mind and yet be wrong. I do not deny that observers may associate particular numerals with particular sensations. I deny only that they have that kind of reason for the association which would make it measurement.

The context shows that I use "true" merely as the dictionary antithesis of "empirical" and not as the dictionary antithesis of "false."

3. In reply to Dr Beatty, Mr Bartlett, Capt. Hume: See paragraph 1.

4. In reply to Mr Guild: Any differences between us appear to me to be differences of emphasis or of expression rather than of substance. I do not know of any further criteria necessary for "measuring the same thing," but am prepared to admit that there may be some that I have overlooked. I should like to stress Mr Guild's statement that the *R*s are complex functions of both sensations and stimuli.

5. In reply to Dr Wright: I agree that *if* a sensation is a magnitude, and *if* mental estimates measure it, *then R* and *S* are not the same thing. But I deny utterly that Dr Richardson has produced any evidence for either part of that hypothesis. The analogy with the basket of apples is incomplete. It would be complete if our estimate of the number of apples depended on whether the 8 apples had been put in the basket originally or whether they had been left after 4 had been taken away from an original 12. Neither Dr Wright nor anyone else meets the point (emphasized when I read the paper) that you must define what you mean by two observers having the same sensation before you combine their observations. Until that definition is given, all analogies with accepted statistical methods are misleading. Finally, see paragraph 12 below.

6. In reply to Mr Smith: I accept most readily his suggestion that mental numerical estimates can be analyzed into recognitions of non-numerical relations. I have some work on this matter in hand.

7. I agree entirely with Dr Shaxby, especially with his third paragraph.

8. In reply to Major Macnair: I have never been able to make up my mind whether I have a mind; I rather think not. But I seem able to interest myself in these discussions without one.

9. In reply to Dr Irwin: I accept entirely his view that there is an analogy—and a helpful analogy—between Keynes's probability (a function of belief) and sensations. But since I am not considering alleged measurement by means of just-perceptible differences, I will not examine his last paragraph.

10. In reply to Mr Maxwell: Surely it is he who begs the question. The question at issue is precisely whether we *are* concerned with measurement of sensations or of stimuli. The remainder of his remarks have already been dealt with implicitly.

11. I have already answered Dr Houstoun's question.

12. Finally, I have realized that there is a very serious error in the last section of my paper. I have there assumed that pairs of sensations similarly related are necessarily represented by pairs of numerals with constant arithmetical difference. This assumption is false; I have fallen headlong into a pit that has trapped many psychologists. I am dealing with the matter elsewhere. So if the method of differences there proposed is, as Dr Wright suggests, identical with the Weber-Fechner method, that method is not merely old, but also fallacious.

536.63:536.62

A METHOD OF MEASURING THE SPECIFIC HEATS OF POOR CONDUCTORS

By W. G. MARLEY, M.Sc.

Communicated by A. F. Dufton, March 4, 1933. Read May 19, 1933

ABSTRACT. A brief review of existing methods of determining specific heats is given with reference to their suitability for poor conductors. The method of cooling, which has received scant attention in the past, is developed to afford an accurate and ready method. This is used to measure the specific heats of typical substances.

§ 1. INTRODUCTION

In connexion with the calculation of heat flow in walls the need has been felt of a simple and rapid method of measuring the specific heats of materials commonly used in building, and the present research was conducted with a view to the development of such a method for routine work.

The measurement of the specific heats of poor conductors is a matter of peculiar difficulty. Such materials are sometimes light and bulky and frequently of a granular or fibrous nature. They are, moreover, generally porous and retain a considerable quantity of moisture, the amount of which greatly affects the thermal capacity.

In order that the determinations shall be of practical value it is necessary that they be made under conditions approaching those obtaining when the material is used for its normal purpose. It will be seen that this requirement prohibits the adoption of some of the usual methods of measurement, and it is therefore proposed, before describing the present work, to review briefly the customary methods.

§ 2. REVIEW OF AVAILABLE METHODS

The method of mixtures is probably the simplest and best known method of calorimetry, though perhaps not the most accurate. It is particularly convenient for determinations of mean specific heats over a range of temperature, but it has been found to be impracticable with substances of the type at present under consideration owing to the change in moisture content during preliminary heating and to the difficulty of obtaining uniformity of temperature throughout the specimen.

In the early days of calorimetry, when accurate temperature-determination was a problem, methods of thermal measurement based upon the change of state of a calorimetric substance were particularly valuable. Bunsen's ice calorimeter and Joly's steam calorimeter are classic examples of apparatus working on this principle, while Dewar has applied the method in measuring specific heats at very low temperatures, using liquefied gases as calorimetric substances.

As the determinations in the present work have to be made at normal temperatures, Bunsen's ice calorimeter would seem suitable; but the difficulty of heating a poorly conducting specimen to a uniform temperature without modifying its water content still remains, and with the thermometers available nowadays the method seems to have little advantage over the method of mixtures, while the apparatus is far more complicated.

The facility with which electrical energy can be measured, conveyed, and suitably dissipated has led to the development of several methods of calorimetry incorporating electrical heating. With such a method the specific heat of water at various temperatures was determined by Callendar and Barnes to a high degree of accuracy and their work probably represents the summit of achievement in the difficult field of calorimetry. Despite the undoubted advantages of electrical methods, research in them has been confined almost entirely to liquids: the author of an article in Glazebrook's *Dictionary of Applied Physics* says (1): "Very little work has been done on the determination of the specific heats of solid substances by the electrical method except for metals. The method, of course, lends itself admirably to the determination of the specific heats of good thermal conductors, but with poor conductors special devices must be adopted to ensure uniformity of temperature throughout the material under test."

A method of measuring the thermal capacities of heavy powders has recently been described (2) by J. H. Awbery and Ezer Griffiths. A measured quantity of energy is introduced electrically and the material is constantly stirred by a special form of stirrer, but no correction is applied for the heat generated in stirring. The temperature-rise is recorded by multiple thermocouples and the thermal capacity of the apparatus is determined from experiments with water.

Griffiths previously described (3) a more complicated apparatus which he used for the accurate measurement of the thermal capacity of materials used in cold-storage insulation. This comprises an adiabatic calorimeter and, in order to obtain uniformity of temperature, the substance is stirred by vanes in a revolving drum. A heating coil imparts a known quantity of energy to the system and a correction is applied for the heat produced in stirring. Loss of heat is reduced to negligible proportions by maintaining an electrically heated jacket always at the same temperature as the drum, and the ultimate temperature-rise affords a measure of the thermal capacity of the drum and its contents.

The maintenance of such an adiabatic condition is by no means easy, and without it a correction has to be applied to allow for the thermal exchange with the surroundings. It would seem possible to utilize this cooling correction as a measure of the thermal capacity of the calorimeter and contents, and experiments have been conducted to develop a method on these lines. The method of cooling has not been used in the past for poor conductors on account of the difficulty of obtaining uniformity of temperature throughout the specimen. Perfect uniformity, however, is not necessary, for initial irregularities tend to even out if the rate of cooling is small [see Appendix], leaving a definite temperature-distribution which persists: the cooling of the specimen is then regular throughout its mass and affords a measure of the thermal capacity.

§ 3. APPARATUS USED IN THE PRESENT WORK

In the present work the specimen is contained in a vacuum flask, 30 cm. deep and 5 cm. in internal diameter, which fits tightly in a metal cylinder immersed in a bath maintained at constant temperature by melting ice (figure 1). The small annular space between the flask and cylinder is filled with water to ensure good thermal contact, and the specimen occupies the flask to a definite level (3·5 cm. from the top) which is conveniently found with a small gauge. A thermometer in the specimen enables the rate of cooling to be determined.

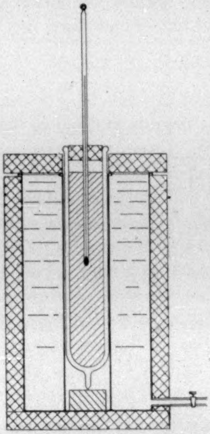


Figure 1. Section of apparatus.

Preliminary experiments with the flask indicated that the rate of transfer of heat was less than 0·003 calorie per second for a difference of temperature of 1° C. between inside and outside, and it was clear that the cooling would be so small that, even with a poor conductor in the flask, temperature-irregularities would vanish after a reasonable time.

§ 4. RADIAL VARIATION OF TEMPERATURE

If the mean temperature of a uniform circular cylinder, cooling slowly by radial flow of heat, is required, it may be found by measurement of the temperature at a point distant $1/\sqrt{2}$ of the radius from the axis. As will be seen in a later section, it is not necessary in the present instance to measure the mean temperature: all parts of the cylinder cool in the same substantially exponential manner, and it suffices to determine the rate of cooling at any one point, preferably in the axis of the cylinder.

§5. VERTICAL SURVEY OF TEMPERATURE

By means of a pair of thermocouples, one of which was situated at one particular point in the flask whilst the other was withdrawn along the axis in stages, the vertical variation of temperature was investigated for various sets of external conditions.

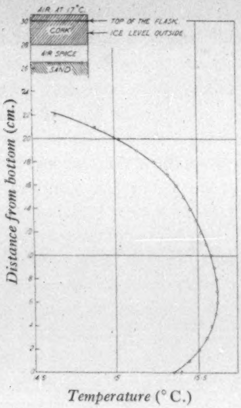


Figure 2. First vertical survey of temperature.

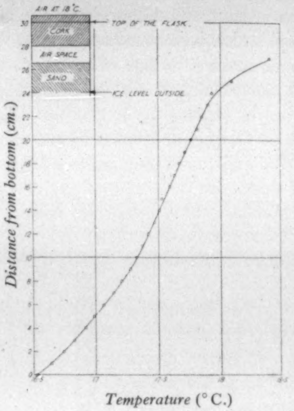


Figure 3. Second vertical survey of temperature.

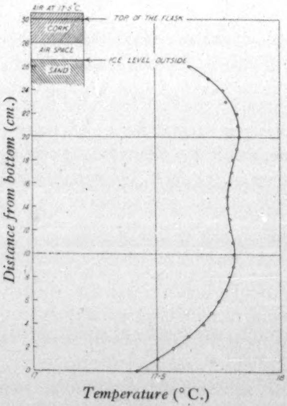


Figure 4. Third vertical survey of temperature.

In the first experiments the flask projected 1 cm. from the top of the ice jacket, whilst the level of the material (sand) inside was some 3·5 cm. below the top of the flask. The temperature was found to vary as shown in figure 2, from which it will be seen that excessive cooling is recorded near the top of the flask.

A second survey was then performed with the flask projecting a further 5 cm. above the ice jacket and the results, shown in figure 3, then indicated that the optimum position has been passed. The discontinuity in the curve at the level corresponding to the top of the ice jacket suggested that the level of the material in the flask ought to be the same as that of the cooling-bath outside. A third survey adequately confirmed this conclusion, and the vertical temperature-variation is seen in figure 4 to be almost zero in the middle section of the flask. In all subsequent work the flask was filled to 3·5 cm. from the top and immersed in the ice jacket to this level.

§6. EFFECT OF VARIATIONS IN LABORATORY-TEMPERATURE

Since 3·5 cm. of flask as well as the cork stopper are exposed to the air of the laboratory, variations in the room-temperature may influence the cooling appreciably. Experiments were conducted to investigate this effect, and two cooling curves were obtained under identical conditions except that the laboratory-temperatures were different. When these curves were plotted on a logarithmic scale of temperature, the rate of cooling was seen to be increased by a definite amount, 1·5 per cent, for every degree by which the flask-temperature exceeded that of the room, and when the curves were replotted with the time intervals between successive points increased in this proportion they yielded parallel straight lines. If the temperature of the flask is θ° C. and that of the laboratory T° C., and if t is the time in seconds, it **θ, T, t**
was found that $\delta t/\delta(\log\theta) = 1650$ when $\theta = T = 13$ and also when $\theta = T = 17$; but when $\theta = 17$ and $T = 12{\cdot}9$, then $\delta t/\delta(\log\theta) = 1555$. Thus

$$\delta t\,[1 + 0{\cdot}015\,(\theta - T)]/\delta \log\theta = 1650$$

in all three cases.

§7. INTERPRETATION OF RESULTS

From experiments such as that just described it was concluded that the curve obtained by plotting the logarithm of temperature against time, after correcting for variations in laboratory-temperature, was practically straight. This is very convenient, for in interpreting the result it is a simple matter to draw a good straight line through the plotted points and so minimize the effect of small errors in individual observations.

With the flask used in the present work the loss of heat amounts to some 160 calories per hour when the temperature-difference between inside and outside is 18° C.: this is lost almost entirely by radiation. A small quantity, not exceeding 10 per cent, is conducted along the glass wall of the flask, and a similar amount is probably transmitted by "carriage"* by the molecules in the residual gas of the vacuum. It seems not unreasonable to suppose that over a limited range of temperature the cooling is according to Newton's law. In this case the slope $\delta t/\delta(\log\theta)$ of the line obtained is proportional to M, the thermal capacity of the flask and contents, because

---

* W. Crookes, *Proc. R. S.* **31**, 239 (1880).

$$-M\,d\theta/dt = k\theta$$

and so, by integration,

$$-M\left[\log_e\theta\right]_{\theta_1}^{\theta_2} = k\left[t\right]_{t_1}^{t_2},$$

that is

$$M = K\delta t/\delta(\log_{10}\theta).$$

In this equation the constant K is a function of the flask alone, and the accurate evaluation of this quantity is an important part of the research.

Since values of $\delta t/\delta(\log\theta)$ are proportional to thermal capacities, they may be added and subtracted in like manner. Calculation is thereby simplified when, for example, the thermal capacity of the flask and thermometer is to be eliminated.

§ 8. METHODS OF MEASURING TEMPERATURE

Since the purpose of the research is to produce not only an accurate but a ready method of measuring specific heat, the method of determining the rate of cooling must be simple. Despite its extremely high accuracy the resistance thermometer is unsuitable as it requires complicated apparatus and has considerable thermal capacity which is a serious disadvantage.

From a thermal point of view a thermocouple is eminently suitable, but it needs an accurate potentiometer. Two pairs of couples were cemented to the flask, and in many experiments readings were made both with these and with an ordinary mercury-in-glass thermometer. The logarithmic cooling curve obtained by measuring the wall-temperature was parallel to that obtained from a mercury thermometer situated in the material at the same level, but the spread of the points was much greater.

The thermal capacity of the mercury thermometer and the fact that heat may be conducted appreciably along the stem may perhaps be cited as possible disadvantages, but the former is not serious in magnitude and the latter vanishes when the observations are corrected for variations in laboratory-temperature. The mercury-in-glass thermometer appears to be the most suitable instrument and was used in obtaining the results given later in this paper.

§ 9. CALIBRATION OF THE APPARATUS

The value of a method of calorimetry is greater if it can be used for absolute determinations. Very few methods, however, permit of this, and consequently the specific heats of most bodies are measured by comparison with a substance of which the thermal capacity is accurately known. With the present apparatus an attempt was made to balance the loss of heat by supplying electrical energy uniformly distributed in the substance, but was abandoned as it was found difficult to maintain steady conditions for the long time necessary for the attainment of thermal equilibrium.

The most accurate comparisons are made when the physical properties of the substances compared are nearly the same, and the possibility of calibrating the present apparatus with solid materials was considered. There are, however, very few solids of which the specific heat is accurately known: the authors of the section dealing with the specific heats of elements in the *International Critical Tables* say(4): "...specific heat data on metals are rarely accurate to better than 1 per cent, an uncertainty of several per cent being not unusual."

An examination of the results obtained by various investigators(5) for the specific heats of otherwise suitable non-metallic substances reveals similar discrepancies of the order of 2 or 3 per cent. It is not a very satisfactory calibration which relies upon such results or even upon a probable value obtained from them.

The specific heat of water is known to a high degree of accuracy and the material is otherwise pre-eminently suitable as a standard. The first calibration was therefore made with the flask containing 542·8 gm. of water and a logarithmic cooling curve, the slope (8380) of which was proportional to the thermal capacity of the water, flask and thermometer, was obtained. In order to eliminate the thermal capacity of the flask and thermometer another curve, of slope 328, was obtained with the flask empty and, as is explained in § 7, the difference (8052) between the slopes corresponded to the difference between the thermal capacities (that is, to the known thermal capacity of the water) yielding a value 0·0674 for the constant K.

In order to obtain consistent results for the empty flask the preliminary heating was performed with the flask full of warm sand, and the thermometer in position; the sand was poured away and the flask quickly corked and inserted in the ice-bath. In the experiments with water the flask was filled to the standard depth given by the small gauge, and the readings were not commenced till two hours had elapsed from the start*, in order that steady conditions might prevail. The curves obtained were corrected for the effects of variation in laboratory-temperature (§ 6) and the slopes were measured at the point corresponding to 18° C. At this temperature the specific heat of water is 0·999 mean cal./gm.

It was thought that convection currents in water might possibly influence the results, and experiments were made to determine whether this was the case. It was found that the flask containing 550 cm.^{3} of coarse sand would also absorb some 220 cm.^{3} of water, and cooling curves were therefore obtained first with the sand alone and secondly with the same sand containing water: the difference between the slopes of the logarithmic curves corresponded to the thermal capacity of the water and yielded a value for the constant K. This experiment was repeated with a different sample of sand and again with fine copper turnings: the various values obtained for the constant are shown in table 1.

In these experiments any convection currents would be greatly reduced by the sand or copper turnings. The fact that the values of K obtained are in excellent agreement with that obtained with water alone indicates that no error is being introduced by convection currents; the apparatus is therefore suitable for the determination of the thermal capacities of liquids.

---

* This procedure was adopted with all the substances studied.

Table 1. Experiments to confirm the calibration

Experiment	Material	Slope $\delta t/\delta(\log\theta)$ (minutes, °C.)	Constant K
3	856·2 gm. sand and 225·1 gm. water in flask	5940	
4	856·2 gm. sand in flask	2587	
(by difference)	225·1 gm. water alone	3353	0·0671
5	838 gm. sand and 220·8 gm. water in flask	5979	
6	838 gm. sand in flask	2675	
(by difference)	220·8 gm. water alone	3304	0·0669
7	1287 gm. copper turnings and 363 gm. water in flask	7440	
8	1287 gm. copper turnings in flask	2062	
(by difference)	363 gm. water alone	5378	0·0675

§ 10. TYPICAL RESULTS

The specific heats of some representative substances have been determined by observation of their cooling in the vacuum flask and the values obtained are shown in table 2.

Table 2. Specific heats of typical substances

Substance	Moisture content (per cent)	Measured specific heat at 18° C. (cal./gm.)
Copper turnings	0·0	$0{\cdot}090_9$
Benzene	0·0	$0{\cdot}41_7$
Potassium chloride	0·1	$0{\cdot}17_1$
,, ,,	0·1	$0{\cdot}17_3$
,, ,,	0·1	$0{\cdot}17_2$
Sodium chloride	0·0	$0{\cdot}20_9$
Cotton wool	3·3	$0{\cdot}30_4$
Charcoal	4·5	$0{\cdot}27_7$
Granulated cork	2·4	$0{\cdot}38_1$

In order that the value of the present method may be more easily assessed table 3, showing results recently obtained by various observers for the materials listed in table 2, is given.

§ 11. ADVANTAGES OF THE METHOD

It will be observed that the range of the values given in table 3 is very large, especially in the case of poor conductors. As this is no doubt due to the difficulties of measurement, it is noteworthy that the present method is as simple and accurate when used with these materials as with good conductors such as copper. The accuracy of the method may be judged to some extent by the consistency of results such as those shown in table 1 for water and the three separate determinations shown in table 2 for a sample of potassium chloride.

Table 3. Specific heats found by various observers

Material	Specific heat	Temperature (°C.)	Observer and reference
Copper	0·094	19	Kolossowsky, *Krak. Anz.* p. 596 (1912)
	0·0911	17	Nernst and Lindemann, *Berl. Sitzber.* p. 1160 (1912)
	0·0909 0·0923	0 23	E. H. and E. Griffiths, *Proc. R. S.* A, **88**, 549 (1913); *Phil. Trans.* A, **213**, 119 (1913)
	0·0915	20	Harpur, *J. Wash. Ac.* **4**, 489 (1914); *Bull. Bur. Stand.* **11**, 259 (1915)
Benzene	0·414	7	Huffman, Parks and Daniels, *J. Am. Chem. Soc.* **52**, 1549 (1930)
	0·4078	20	Williams and Daniels, *J. Am. Chem. Soc.* **47**, 1490–1503 (1925)
	0·416	20	Dejardin, *Ann. Phys.* (9), **11**, 253 (1919)
	0·410	20	Tréhin, *Ann. Phys.* (9), **15**, 246 (1921)
Cotton-wool	0·319	—	Dietz, *Lpz. Monatsh. f. Textilind.* **27**, 85 (1912)
	0·362	0 to 100	Ottolenghi, *Mem. di Turino* (2), **57**, 97 (1907)
	0·280– 0·283	0 to 34	Meltzer, Dr. Dissert., Darmstadt (1928)
Charcoal, 6·89 per cent water	0·299	25	Griffiths, *Proc. Phys. Soc.* **33**, 335–361 (1921)
Granulated cork, 3·45 per cent water	0·438	25	Griffiths, *Proc. Phys. Soc.* **33**, 335–361 (1921)
Sodium chloride	0·2146	0	R. Weber, *Séanc. Soc. Neuchâtel*, 28 Marz. 1895; *Arch. sc. Phys.* (3), **33**, 590 (1895)
	0·2036	0 to 19·6	Brönsted, *Z. Elch.* **20**, 554 (1914)
	0·2078	24	Russell, *Phys. Z.* **13**, 59 (1912)
	0·2069	17 to 99	Magnus, *Phys. Z.* **14**, 5 (1913)
Potassium chloride	0·1652	58	Nernst and Lindemann, *Berl. Sitzber.* p. 1160 (1912)
	0·1616	0 to 19·6	Brönsted, *Z. Elch.* **20**, 554 (1914)
	0·1661	23	Russell, *Phys. Z.* **13**, 59 (1912)
	0·1654	16 to 99	Magnus, *Phys. Z.* **14**, 5 (1913)

With an ordinary mercury thermometer graduated in tenths of degrees the accuracy of reading is such that the plotted points are well aligned, and experience has shown that the slope of the line through the points can be determined within about 0·5 per cent. As the results are generally calculated from the difference between two experiments the ultimate error should be less than 1 per cent, and a comparison of the results quoted in tables 2 and 3 would tend to confirm this. Moreover with poor conductors such as sodium chloride the agreement is no less than in the case of copper, and it is concluded that the accuracy is not greatly dependent upon the thermal capacity or the conductivity of the material. The method is therefore submitted as an accurate and ready method of measuring at laboratory-temperatures the specific heats of liquids and granular or fibrous materials of low conductivity. It is possible that the method could be extended to permit the determination of specific heats at other temperatures; for measurements in the neighbourhood of 100° C., for instance, a steam jacket round the flask would be convenient. Such work, however, is somewhat outside the scope of the present research, which is confined to measurements at normal temperatures.

§ 12. ACKNOWLEDGMENT

In conclusion, the author wishes to thank Mr A. F. Dufton, of the Building Research Station, for suggesting the method and for his valuable encouragement and advice.

REFERENCES

(1) *Dict. of Appl. Phys.* **1**, 37, § 8.
(2) *Proc. Phys. Soc.* **42**, 71, 232 (1930).
(3) *Proc. Phys. Soc.* **33**, 355 (1921).
(4) *International Critical Tables*, **5**, 92 (1st edition, 1929).
(5) Landolt-Börnstein. *Physikalisch-Chemische Tabellen*, **2**, 1252 (5th edition, 1923).

APPENDIX. THE DECAY OF TEMPERATURE-IRREGULARITIES

c In a completely heat-insulated cylinder of length c, if the temperature be uniform over any plane at right angles to the axis and the initial temperature-distribution be of the form

A, p, x

$$\theta = A \sin \frac{p\pi x}{c},$$

t then, after time t, the temperature at the mid-point of the cylinder will be

a

$$\theta_t = A\left\{\frac{2}{p\pi} - \sum_{n=1}^{\infty} \frac{4p}{\pi(4n^2 - p^2)} . \cos n\pi . e^{-4\pi^2 a^2 n^2 t/c^2}\right\},$$

when p is odd and a^2 is the diffusivity. From this formula values of $(\theta_t - \theta_\infty)$ were calculated for a cylinder of granulated cork, for which $a^2 = 0{\cdot}0032$ c.g.s.u. The values of $(\theta_t - \theta_\infty)$ for an extreme initial variation of 1° C. are shown in the table.

p	$(\theta_t - \theta_\infty)$ $t = 2$ hr.	$(\theta_t - \theta_\infty)$ $t = 3$ hr.	$(\theta_{2\text{ hr.}} - \theta_{3\text{ hr.}})$
1	+ 0·099	+ 0·048	+ 0·051
3	− 0·089	− 0·043	− 0·046
5	− 0·035	− 0·017	− 0·018
7	− 0·023	− 0·011	− 0·012

With the experimental procedure described in the paper, observations of cooling throughout the third hour would be in error by the amount shown in the last column, an error of the order of 1 per cent when p is unity. It is clear that the error decreases as p (the number of peaks) increases and, furthermore, when the number of peaks is even the error becomes zero.

Since the radius of the flask is only one-tenth of the length, any radial irregularities of temperature will disappear long before the axial variations become insignificant, and a detailed investigation of these is therefore unnecessary.

By adequate mixing of the material the initial irregularities can be kept down to 1° C. The error, therefore, is likely to be very small and can be still further reduced by taking a mean of two or more experiments. It remains to point out that in the present research observations were not made till the third hour, and in most instances two or more curves which gave results in very close agreement were obtained.

DISCUSSION

Mr W. C. S. **Phillips**. I am particularly interested in this method of measuring specific heat as applied to poor conductors and insulators. The author has taken care to arrange conditions so as to obtain a uniform axial temperature near the middle of the flask, but I should be glad to know to what extent the radial variation in temperature is uniform. What method was adopted for initially heating the materials? If the initial temperature-distribution is very irregular after such heating, was it necessary to allow some time to elapse before taking readings of the thermometer?

Mr J. H. **Awbery** said that some thermometers would read a falling temperature correctly if tapped. The author's experience was not unique in this respect, but whether a thermometer behaved thus or not was a matter of luck.

Author's reply. In reply to Mr Phillips: I would refer to §§ 4, 9, in which I have pointed out that, when the specimen is cooling exponentially, the position of the temperature-measuring device does not affect the slope of the logarithmic cooling curve obtained, although there may be a considerable drop in the temperature along a radius, amounting in some instances to one or two degrees. Slight heating was necessary to raise the initial temperature of the specimen a few degrees above that of the laboratory. This was done in a metal box while the specimen was stirred continuously, and it was found possible to keep the variations in temperature down to within 1° C. No observations were made till the cooling had proceeded for at least two hours (see § 9), and it is shown in the appendix that initial irregularities will then have become insignificant.

With regard to Mr Awbery's remarks I would like to say that I have used two thermometers in this work and both have been beyond reproach in the matter of freedom from sticking: this could be seen to some extent in the excellent alignment of the points on the cooling curves.

537·322.4

THERMOMAGNETIC HYSTERESIS IN STEEL

By W. Y. CHANG, M.S. (Yenching), and WILLIAM BAND, M.Sc.,
Professor of Physics, Yenching University, Peiping, China

Received January 3, 1933. *Read in title May* 20, 1933

ABSTRACT. The temperature variation of a new hysteresis of the thermomagnetic electromotive force in a steel wire is described. The hysteresis is of a negative or abnormal form, with a maximum amplitude of about 2 μV. between up and down branches. The accuracy of the apparatus and method is critically examined, and an error of more than 0·5 μV. in any reading is considered to be unlikely.

A qualitative explanation of the phenomenon is given in terms of Gerlach's* theory of spontaneous magnetization, and Broili's† results for nickel are discussed from the point of view of that theory.

1. INTRODUCTION

Several papers have recently been published describing the thermomagnetic e.m.f. in nickel and iron wires, and a hysteresis of the effect has been discovered for both metals. Band and T'ao announced‡ a hysteresis of the e.m.f. in iron, but described no detailed properties of the phenomenon. After the present work had been commenced, Heinz Broili§ described the temperature variation of the hysteresis of a similar e.m.f. in pure nickel wires. The nickel hysteresis was a normal type with small retentivity and coercive field, but the iron curve was peculiar in that a permanent remanent e.m.f., which never disappeared during several cycles, seemed to have been produced by the field.

Unfortunately the curve published by Band and T'ao showed signs of a vagrant shift of zero e.m.f. during the cycle, and there was not much detailed investigation into this source of error. The results given in the present paper were obtained with apparatus similar to that used previously in these laboratories, and appear to have established the hysteresis on a more secure basis. The results are numerous and the various sources of error have been traced out carefully until a satisfactory self-consistency has been attained.

The experimental arrangement used in the present work is similar in principle with that used by Sir William Thomson‖ when the longitudinal thermomagnetic e.m.f. was first discovered. That used by Broili was different in that a uniform temperature is maintained throughout each part of the specimen wire over which a non-uniform magnetic field exists. Broili's apparatus gave the pure longitudinal effect, and we should expect the present results to be somewhat more complex though not beyond analysis. In the present work the potential leads (of the same material as the sample) were taken transversely to the field through small holes in the solenoid and were thus non-uniformly magnetized by the field even though they were not uniform in temperature.

---

* Becker, *Z. f. Phys.* **62**, 253; **63**, 660 (1930); Gerlach, *Ann. d. Phys.* **8**, 649 (1931).

† Heinz Broili, *Ann. d. Phys.* **14**, 3 (1932).

‡ *Proc. Phys. Soc.* **44**, 166 (March, 1932).

§ Heinz Broili, *Ann. d. Phys.* **14**, 3 (1932).

‖ *Math. and Phys. Papers*, **2**, 267–307.

2. ACCURACY OF THE APPARATUS

A water-cooled solenoid of the Moullevigen* form gave fields up to 380 G. uniform to 0·1 per cent over a length of 40 cm. A heating coil of nichrome wire wound non-inductively gave temperatures up to 900° C. uniform over 20 cm. and controllable to within 0·4° C. A water-cooling jacket, also in the axis of the solenoid, gave uniform cool temperatures over 20 cm. which were found to remain constant within 0·1° C. for periods of one hour†. Transverse leads of the same material as the longitudinal wire were taken out from the centres of these two uniform-temperature stretches and led through the solenoid into two Dewar flasks containing melting ice, where junction with the copper leads was effected. A Leeds Northrupp K-type potentiometer measured the e.m.f. between these two leads to within 0·5μV., against a standard cell placed in a thermostat maintaining a constant temperature to within 0·01° C. The last change in temperature would involve a change in the standard voltage of 0·406μV. The temperature of the hot part was measured by means of an iron-platinum couple, of which the iron element was the part of the sample projecting from the hot oven through the end of the solenoid, figure 1. In every case the wire was kept under constant tension by the application of a weight of 2 kg.

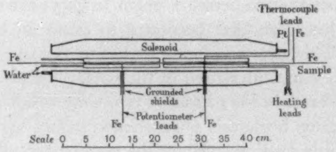


Figure 1. Section through the water-cooled solenoid, heating-coil and water-jacket. The Dewar flasks, potentiometer, galvanometer, etc., are omitted.

After the work had been completed we realized that errors might have been introduced into the temperature-measurements by the magnetization of one of the thermo-elements. In our case iron—the specimen itself—was used against platinum. If the temperature of the iron element varied appreciably in a strong field the thermomagnetic e.m.f. would be produced in the thermocouple, and only 0·2μV. would in our case be required to produce an error of 1° C.

---

* *J. d. Phys.* **7**, 466 (1898).

† The water is obtained directly from an artesian well of considerable depth on the university campus, and its temperature is therefore almost independent of daily variations in surface temperatures.

A very searching test was therefore carried out to check this error. The iron wire was stretched as before down the axis of the solenoid and a piece of platinum wire soldered on at the centre of the heating coil. Another platinum wire and a copper wire were also attached at the same point to form an independent non-magnetic thermocouple to test for variations of temperature. Tests were then made over a complete cycle of the solenoid field at three different temperatures near 160°, 500° and 900° C. respectively. The reading of the platinum-iron junction was kept constant by adjustment of the heating current, and any variations in the other couple were noted. Variations of temperature of 1° C. could easily have been detected in the galvanometer reading, but no trace was found in fact at any of the temperatures. Even sudden changes in the field produced no detectable changes as between the readings of the two thermocouples, which were connected to two independent galvanometers of similar sensitivity.

We can explain this null result rather easily in our case. The iron element was kept at a uniform temperature throughout the strong part of the field, and not until the field is smaller does the temperature begin to vary; the e.m.f. produced must therefore have been less than that necessary to cause an error of 1° C. in the temperature reading. This error was found by test to correspond to less than 0·5μV. in the thermomagnetic e.m.f. measured in the potentiometer.

Had there been an error in the measured temperatures of about 5° C. due to the magnetic field, a spurious hysteresis phenomenon would have occurred: in maintaining the thermocouple reading constant the temperature would have been taken through a cycle during the field cycle, and the thermomagnetic e.m.f. values obtained would not have been those corresponding to some one temperature-difference between hot and cold ends; there would have been variable errors amounting to the order of several microvolts. It thus seems that accuracy to less than 1° C. is desirable for the temperatures at both ends of the specimen, and that this accuracy is actually attained in the present work.

3. RESULTS

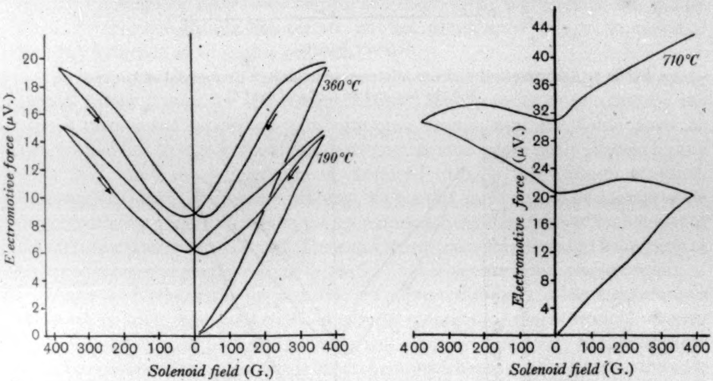
Analysis of iron sample. The wire investigated in these experiments was thermo-element metal manufactured by the Kahlbaum Company. The diameter was uniformly 0·57 mm. Two independent chemical analyses showed that the metal contained only 98·97 per cent of iron, the remaining 1·03 per cent being chiefly composed of carbon, manganese and sulphur, with traces of silicon and phosphorus: the latter were not exactly determined.

The ordinary hysteresis properties of the wire were determined by standard methods. It showed magnetic saturation under fields of 75 G. at 23° C.; the intensity of magnetization being 1110 c.g.s. units. There was retentivity of about 77 per cent. At 275° C. saturation was reached in fields of 30 G., the intensity of magnetization being 740 c.g.s. units; and there was retentivity of 44 per cent. The coercive field necessary to reduce magnetization to zero after saturation was 15 G. at 23° C. and about 4 G. at 275° C.

At a later stage we hope to investigate the various related properties of the same specimen; magnetic resistance-change, specific-heat changes with magnetization, etc.

Hysteresis of the e.m.f. Figure 2 shows the hysteresis curves obtained when the hot end of the wire was at the temperatures respectively of 190°, 360° and 710° C.; in each case the cold end was between 19° and 20° C. The e.m.f. has been recorded as positive when it is directed from the hot end to the cold end of the specimen.

The initial e.m.f. in zero field was found in general to be about the same for any given temperatures after separate demagnetization processes. But sometimes it would differ by considerable amounts, even changing sign. Normally the initial e.m.f. would be positive from hot to cold end, but sometimes it would be in the opposite sense. This was probably due to incomplete demagnetization, as will be pointed out later in the discussion of the results. But the general form of the hysteresis was found to be independent of this initial discrepancy. A sample curve obtained when the initial e.m.f. was negative is shown in figure 4. After the first quarter-cycle there is not much difference from the curves of figure 2(*a*).



(*a*) (*b*)

Figure 2. (*a*) Hysteresis of the thermomagnetic e.m.f., with the cold end of the wire at 19·5° C. and the hot end at 190° and 360° C. (*b*) Hysteresis with the cold end at 18·5° C. and the hot end at 710° C.

Effect of the transverse leads. To estimate the effect of the transverse leads on the hysteresis the longitudinal steel wire was removed and in its place a copper wire was stretched along the axis of the solenoid; the same steel leads to the potentiometer being used as before. The e.m.f. produced by the field was then determined as before. It may be permissible to subtract the e.m.f. found in this way from the total e.m.f. found before, and to call the difference the pure longitudinal e.m.f.: but this procedure seems to require too many assumptions to be rigorous. At least it gives us a qualitative idea of the facts, however.

Figure 3 shows the cycles obtained for two temperatures, respectively 200° and 350° C. at the hot end and 17·5° C. at the cold end in both curves. It will be immediately noted that there is no trace of a hysteresis loop, but that the field definitely introduces a permanent remanent e.m.f., which remains constant after the first quarter-cycle. This remanent e.m.f. remains constant throughout the field cycle. It increases with temperature, but not quite as rapidly as the remanent e.m.f. found in the total e.m.f., figure 2(*a*). We may therefore assume that the permanent remanent e.m.f. is due partly, if not entirely, to the transverse leads, while the hysteresis loop is purely a longitudinal effect.

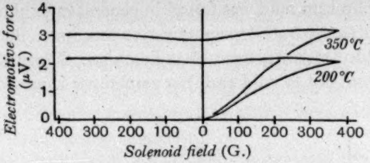


Figure 3. Complete cycles of e.m.f. in transverse leads, with the cold end at 17·5° C., and the hot end at 200° and 350° C.

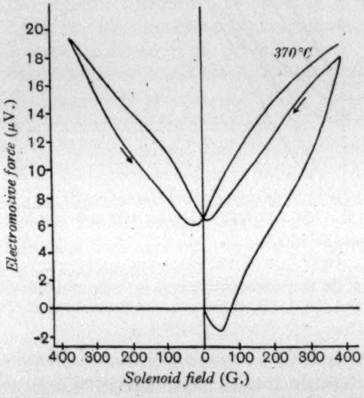


Figure 4. Hysteresis of the thermomagnetic e.m.f., when the initial e.m.f. in zero field is negative. Cold end at 22·5° C. and hot end at 370° C.

Obviously it is desirable to perform the experiments without having any transverse leads, and some new apparatus designed for this purpose has already been constructed. The results will be published in another paper, because the principle of the arrangement is quite different from the present one.

4. DISCUSSION OF RESULTS

The theory of spontaneous magnetization. Although there is still a great deal of confusion in the literature between the idea of intrinsic field and that of spontaneous magnetization, the particular interpretation of the latter given by Becker* will serve to give at least a qualitative explanation of our hysteresis curves. According to Becker, two distinct phenomena occur when a metal undergoes ferromagnetization: (*a*) the reversal process in which magnetic vectors directed originally opposite (or nearly so) to the external field are suddenly reversed in sense without change of direction; and (*b*) the turning process in which vectors nearly parallel to the field are turned more nearly parallel. The latter process is supposed by Becker to be effective for magnetic resistance-decrease and magnetostriction phenomena, and by Broili† for thermomagnetic phenomena; but the reversal process is not supposed to have any influence at all in this respect.

Gerlach‡ considers that the turning process is essentially a change of the spontaneous magnetization (or true magnetization); and in order to account for the various phenomena connected with resistance change near the Curie point he assumes that this change in spontaneous magnetization is more easily effected by any given field when the temperature is increased towards the Curie-point value. Applying this idea to the present problem, we see that there should be a greater true magnetization (a greater change in the spontaneous magnetization) at the hot end of the specimen than at the cold end. The e.m.f. observed is then directed from parts of higher spontaneous magnetization to parts of lower spontaneous magnetization.

If now we further make the plausible assumption that at the colder temperatures there will be some hysteresis of the change in spontaneous magnetization, whereas at the hot end no such (or less) hysteresis will occur, we find a very simple explanation of our hysteresis results. We must first emphasise that our hysteresis curves are all remarkable in that they are negative hystereses. The e.m.f. in an increasing positive or negative field is always greater than the e.m.f. in decreasing positive or negative field. And this is explained by the above hypothesis; for in a decreasing field the spontaneous magnetization of the cold end does not decrease as rapidly as the (greater) true magnetization at the hot end, and therefore the difference is less than for the increasing field. The abnormal hysteresis curves may thus be taken as a remarkably interesting proof of the spontaneous magnetization theory and of Gerlach's views in relation to it.

It is interesting to note that on plotting the square of the intensity of magnetization as a function of the field for the two temperatures, and then finding the difference curve between the two graphs, we obtain a hysteresis curve of quite a different form from that for the thermomagnetic e.m.f. This shows that the total magnetic energy is not the significant factor for the phenomenon. We can similarly satisfy ourselves that the induction in the wire is non-significant.

---

* *Z. f. Phys.* **62**, 253; **63**, 660 (1930).

† *Ann. d. Phys.* **14**, 3 (1932).

‡ *Ann. d. Phys.* **8**, 649 (1931).

We have noticed that a change in tension of the wire produces an e.m.f. even when the magnetic field is kept at zero, and that there is a hysteresis of this e.m.f. also. This is mentioned here only as further elucidation of the spontaneous-magnetization theory; more work is being done and results will be published later. Here we point out that tension will turn the magnetic vectors without changing their magnitude, and will not cause any reversal of their sense. This has been fully discussed by Gerlach and his collaborators* in connexion with the change of resistance produced by tension. It will thus be realized that the existence of hysteresis in the e.m.f. produced by tension is a satisfactory indication that the assumptions made above as regards hysteresis of the turning process are valid.

Phenomena at the Curie point. The Curie point for the wire used has not yet been determined with any great accuracy; but we have found that the thermomagnetic e.m.f. reaches saturation in a constant field when the temperature at the hot end is near 750° C. We may assume, in the light of Broili's† work, that the Curie point is close to this temperature. An estimate of the Curie-point temperature was also obtained from three separate cooling curves against a platinum-copper thermocouple. These all agreed in giving the temperature of recalescence as 735° C., and the result is probably more accurate than that derived from the saturation temperature. But too much reliance cannot be placed on it; Gerlach has defined the Curie point in quite a different way‡, and his value may be different. In any case, however, we see that the curve for 710° C. shown in figure 2(*b*) corresponds to a temperature very near the Curie point at the hot end. This may account for the anomalous form, but no further explanation has as yet been found. We hope to investigate later.

Comparison with previous results. Broili, in the work already quoted, did not notice any hysteresis in iron below 500° C. The metal which he used was, however, much purer and softer than that used here; our material was a rather hard steel, and the occurrence of hysteresis may be more likely in it. It is interesting to note, on the other hand, that Broili found two distinct phenomena corresponding with the two different initial e.m.f. states mentioned in the present paper.

Generally Broili found curves which were very similar to the first quarter-cycles shown in figure 4. But if the iron was heated up to above 600° C. before the beginning of the cycle and allowed to cool, the cycles became like those in our figure 2(*a*). Broili interpreted this as due to some kind of "recrystallization" of the iron at temperatures above 600° C. But the curves shown in figure 2(*a*) were found by us in steel in which no recrystallization had taken place; the heating process was at no time given to the specimen. It therefore seems that a more careful investigation into the phenomenon is required before Broili's interpretation can be accepted.

It seems to us that incomplete demagnetization may account for the temporary negative e.m.f. obtained in the curves for small fields like that in figure 4. This would mean that Broili's results for his "non-recrystallized iron" are erroneous;

---

* See, e.g., Erno Englert, *Ann. d. Phys.* **14**, 589 (1932).

† *Ann. d. Phys.* **14**, 3 (1932).

‡ Gerlach and Schneiderhan, *Ann. d. Phys.* **6**, 772 (1932).

unless the fact that his is soft iron will account for the difference. At least we obtain curves with our hard steel which are similar to Broili's for the recrystallized iron; and probably the heating process of Broili does little more than destroy the magnetization left by the insufficient demagnetization process.

Broili describes the hysteresis of the e.m.f. in pure nickel wires, and we note that his curves are of the normal or positive form; the e.m.f. is greater in absolute value for decreasing positive or negative fields than for increasing fields. This results in a contradiction with the qualitative theory put forward to explain the negative hysteresis we found in steel. It is true that the e.m.f. in nickel is opposite in sense to that in iron, being directed from cold to hot temperatures; but nevertheless the absolute value of the e.m.f. should undergo the negative hysteresis in both metals.

In this connection we should like to point out that Broili appears to have neglected a probable source of error in his work. In the researches on nickel Broili used a copper-constantan thermocouple to control the hot temperature, and constantan usually contains about 40 per cent of nickel. The thermomagnetic e.m.f. developed in nickel is rather higher than that in iron, as his own work also showed. Now since a rapid temperature-drop exists in the constantan wire as it emerges from the heating oven in the field of the solenoid, one would expect a considerable e.m.f. introduced into the thermocouple circuit by the influence of the magnetic field.

Broili does not mention this, and apparently no tests were made to check it. It is possible therefore that there is in his results a spurious hysteresis error of the type discussed earlier in the present paper. It is proposed to go over the work with nickel wires in these laboratories, with this possible error in mind.

621.396:621.54

A NOTE ON INTERFERENCE TONES IN SUPERHETERODYNE RECEIVERS

By W. F. FLOYD, B.Sc.

Communicated by Dr Allan Ferguson, February 17, 1933.
Read May 19, 1933

ABSTRACT. The question of interference tones, in the case of a superheterodyne receiver, presents certain features not encountered in the case of non-heterodyne types of receivers. Briefly, the problem involves (1) the reception of at least three signals, (2) double detection, and (3) a filter action between the two detectors. In the case of rectification by detectors with generalized characteristics, quantitative analysis is extremely complex. The form of the result, however, shows how large is the number of possible sources of interference tones. The specific case of square-law rectification is considered also.

We shall consider a single-dial-control superheterodyne receiver in which
the local-oscillator frequency is always greater than that of the desired
E signal. The voltage E at the grid of the first detector will be composed of
E_1, E_2 three fundaments, the desired signal voltage E_1, the local-oscillator voltage E_2, and
E_3 E_3 due to the presence of an interfering signal. Then we may write

$$E = E_1 + E_2 + E_3 \qquad \text{......(1),}$$

e_1 where

$$E_1 = e_1 \cos \omega t \qquad \text{......(2),}$$

e_2

$$E_2 = e_2 \cos (\omega + n) t \qquad \text{......(3),}$$

e_3

$$E_3 = e_3 \cos (\omega + f) t \qquad \text{......(4),}$$

f, n and where f may have any value, positive or negative, and n is supersonic and bears the same order of relation to ω as angular audio (modulation) frequencies bear to n. Tuning-circuit effects are assumed to be implicitly expressed by these values. Substituting equations (2), (3), and (4) in equation (1), and applying the well-known trigonometric transformations, we have

$$E = V \cos (\omega t + \phi) \qquad \text{......(5),}$$

V where

$$V^2 = e_1{}^2 + e_2{}^2 + e_3{}^2 + 2e_1 e_2 \cos nt + 2e_1 e_3 \cos ft + 2e_2 e_3 \cos (n - f) t \qquad \text{......(6),}$$

ϕ and

$$\phi = \tan^{-1} \frac{e_2 \sin nt + e_3 \sin ft}{e_1 + e_2 \cos nt + e_3 \cos ft} \qquad \text{......(7).}$$

CASE 1. GENERAL RECTIFIER

We shall assume that the (current, voltage) characteristic of the first detector is of the form

$$i = a_0 + a_1 e + a_2 e^2 + \ldots + a_r e^r + \ldots \qquad \ldots\ldots(8),$$

a_r

where i is the output current, e the input voltage, and the a's are constants. The output current for an input voltage represented by equation (5) is then

i, e

$$i = a_0 + a_1 V \cos(\omega t + \phi) + a_2 [V \cos(\omega t + \phi)]^2 + \ldots + a_r [V \cos(\omega t + \phi)]^r + \ldots\ldots(9).$$

Now the output circuit of this valve contains selective devices (usually band-pass filters) tuned to select, from the output current, only those components of angular frequency between $n + \epsilon$ and $n - \epsilon$, where ϵ is an angular audio frequency and ϵ/π is the width of the tuning curves of the selective devices. Rewriting equation (9) and expanding the powers of the cosines in terms of multiple angles we have

ϵ

$$\begin{array}{llll} i = a_0 + a_1 V \cos(\omega t + \phi) & & & \\ \tfrac{1}{2} a_2 V^2 & + \tfrac{1}{2} a_2 V^2 \cos 2(\omega t + \phi) & & \\ \quad + \tfrac{3}{4} a_3 V^3 \cos(\omega t + \phi) & & + \tfrac{1}{4} a_3 V^3 \cos 3(\omega t + \phi) & \\ \tfrac{3}{8} a_4 V^4 & + \tfrac{1}{2} a_4 V^4 \cos 2(\omega t + \phi) & & + \text{etc.} \\ \quad\ldots & \ldots & \ldots & \ldots \\ \dfrac{r(r-1)\ldots(r/2+1)}{2^r . r/2!} a_r V^r + \text{terms in } \cos 2(\omega t + \phi), \cos 4(\omega t + \phi), \text{etc.} & & & \\ \qquad\qquad + \text{terms in } \cos(\omega t + \phi), \cos 3(\omega t + \phi), \text{etc.} & & & \ldots\ldots(9a). \end{array}$$

Here r is even only.

Only terms from the first column of equation (9a) will be selected by the selective devices. All other terms have angular frequencies of the order of ω and multiples of ω, and will not be taken into account in the present treatment. Considering only terms in the first column, we have

$$I = A_2 V^2 + A_4 V^4 + A_6 V^6 + \ldots + A_s V^s + \ldots \qquad \ldots\ldots(10),$$

I, A_s

where s is even and the A's replace the coefficients in equation (9a). The constant term a_0 has been omitted, since it does not contribute to the useful output. As we shall now be concerned only with qualitative results we need not consider the values of the As. Substituting equation (6) in (10), we have

$$\begin{aligned} I = {} & A_2 [e_1^2 + e_2^2 + e_3^2 + 2e_1 e_2 \cos nt + 2e_1 e_3 \cos ft + 2e_2 e_3 \cos(n - f)t] \\ & + A_4 [e_1^2 + e_2^2 + e_3^2 + 2e_1 e_2 \cos nt + 2e_1 e_3 \cos ft + 2e_2 e_3 \cos(n - f)t]^2 \\ & + \text{etc.} \qquad \ldots\ldots(11). \end{aligned}$$

Expanding the general term in equation (11) by means of the multinomial expansion (see appendix) we see that equation (11) is composed of terms whose angular frequencies are exactly represented in the following two-dimensional array

$$\left.\begin{array}{ccccc} —, & f\ , & 2f\ , & 3f\ , & \cdots \\ n, & n \pm f, & n \pm 2f, & n \pm 3f, & \cdots \\ —, & 2n \pm f, & 2n \pm 2f, & 2n \pm 3f, & \cdots \\ —, & 3n \pm f, & 3n \pm 2f, & 3n \pm 3f, & \cdots \\ —, & \cdots & \cdots & \cdots & \\ —, & \cdots & \cdots & \cdots & \end{array}\right\} \qquad \ldots\ldots(12).$$

p, q η, ϵ

By giving f an appropriate value, namely that given by $pf = qn \pm \eta$ where p and q are integers, and $\eta < \epsilon$, the various terms in the array actually contributing to the output current may be picked out. Thus, in the case where $p = 1$, $q = 2$, we see that the following terms contribute towards the output: $(2n - f)$, $(n - 2f)$, $(3n - 2f)$, $(5n - 2f)$, $(5n - 3f)$, $(7n - 3f)$, and so on.

ξ

The term of angular frequency n in equation (12), standing alone in the first column, is always present in the output, and is the term representing the output when $E_3 = 0$; that is to say, when no interfering signal is present. All the other terms in equation (12) contributing to the output, when a value is assigned to f, have angular frequencies of either $n + \xi$ or $n - \xi$, where

$$\xi = \alpha . \eta < \epsilon \qquad \text{......(13).}$$

α

and α is an integer.

$\mathscr{E}$

Thus the voltage $\mathscr{E}$ applied to the grid of the second detector, on the assumption that the intermediate frequency amplifier does not introduce frequency distortion between the limits $n + \epsilon$ and $n - \epsilon$, is of the form

$$\mathscr{E} = P \cos nt + Q_1 \cos (n + \xi)\, t + Q_2 \cos (n - \xi)\, t \qquad \text{......(14),}$$

P, Q_1, Q_2

where P depends on powers of e_1 and e_2 only, and Q_1 and Q_2 on powers of e_1, e_2, and e_3.

Assuming that the action of the second detector also is represented by the general relation of equation (8), substituting equation (14) in equation (8), and expanding the series so obtained in the same manner as previously, we see that the audio output contains a number of whistling tones, the angular frequencies of which are integral multiples of ξ. The relative amplitudes of these are as follows:

Angular frequency	ξ	2ξ	4ξ	8ξ ...
Amplitude proportional to	$P(Q_1 + Q_2)$	$Q_1 Q_2$	$Q_1^2 Q_2^2$	$Q_1^4 Q_2^4$...

These whistling tones are additional to the bands of interference tones due to the various combinations of the modulation frequencies of E_1 and E_3. In actual practice, when interference is being experienced with a one-dial-control superheterodyne receiver, the frequencies ω, f, of the wanted and unwanted signals remain constant, and n varies slightly owing to inaccuracies in the ganging between signal-input and oscillator circuits.

Δn

Suppose that an interfering signal is producing whistling tones in the output of a receiver, and that the receiver-tuning control is adjusted so that the signal-input circuit is tuned over a range equal to the band-width of the desired signal. Suppose also that the angular frequency of the oscillator changes by an amount Δn during this operation. Now in the relation

$$pf = qn \pm \eta,$$

$\eta\Delta$

the value assigned to f is independent of variation in n. When n varies by Δn, η also must vary by $\Delta\eta$ in order that this relation may be true, and we have

$$q . \Delta n \pm \Delta\eta = 0 \qquad \text{......(15).}$$

$\Delta\xi$

Hence ξ and the multiples of ξ vary by an amount given by

$$\alpha q . \Delta n \pm \Delta\xi = 0 \qquad \text{......(16),}$$

That is to say, the whistling tones vary slightly in pitch. The amount of variation depends, of course, mainly on the accuracy of the ganging of the input and oscillator circuits. As a typical case consider a receiver designed to cover the wave-lengths from 200 to 600 metres, that is to say, covering one hundred channels each of 10 kc./sec. width, so that rotation of the condenser scale through 0·01 of the total scale reading is sufficient to tune completely through a station. The sections of a good modern ganged condenser are generally matched to within $\frac{1}{2}$ per cent or 1 μμF., whichever is the less. Taking this figure, it is clear that $\Delta C/C$ is of the order of 10^{-4}, where ΔC is the misalignment error between two sections, introduced by rotation of the condenser through a small amount. The variation in ξ is given, as before, by ΔC

$$\alpha q . \Delta n \pm \Delta \xi = 0,$$

where

$$\Delta n + \tfrac{1}{2} (\Delta C/C)\, n = 0.$$

At a wave-length of 500 metres $n = 12\pi \times 10^5$ radians per second, and we have

$$\pm \alpha q \, \tfrac{1}{2} . 10^{-4} . 12\pi . 10^5 = \Delta \xi,$$

or

$$\pm 60\pi \, \alpha q = \Delta \xi.$$

Therefore, in this case, the fundamental whistling tone varies in pitch by an amount of $\pm 30\alpha q$, where α and q are integers. In practice the pitch is found to vary by amounts of the order of 300, giving a value of the order of 10 to the product αq.

The whistling tones occur at several places around the tuning scale in the majority of commercial models of superheterodyne receivers when they are operated in the vicinity of a broadcasting station, and the writer has yet to meet an instrument which does not suffer from this trouble in some degree. The actual magnitudes of the tones cannot be determined until the various coefficients in the first and second detector functions are known. It is clear, however, that the amplitude of the fundamental tone, of angular frequency ξ, is greater than the amplitudes of the overtones of ξ.

CASE 2. SQUARE-LAW RECTIFIER

Assuming that the first detector (current, voltage) characteristic is of the form $i = kV^2$, and putting $f = \pm n \pm \epsilon$, we find that the terms selected from its output current by the intermediate frequency selective circuits are as follows:

$$I = k_1 [2e_1 e_2 \cos nt + 2e_1 e_3 \cos (n \pm \epsilon) t] \qquad \text{......(17)}.$$

I, k_1

If we put $f = 2n$, we have the simple case of second channel interference, and the amplitude of the second term in equation (17) becomes $2e_2e_3$.

If no distortion occurs in the intermediate frequency amplifier, the voltage applied to the grid of the second detector will be proportional to I in equation (17), and if this also operates as a perfect square-law rectifier, the audio output terms will be given by

$$k_2 I_A = 2e_1{}^2 e_2{}^2 + 2e_1{}^2 e_3{}^2 + 4e_1{}^2 e_2 e_3 \cos \epsilon t \qquad \text{......(18)}.$$

k_2, I_A

If E_1 and E_3 are both modulated, the first term in equation (18) contains the desired signal plus harmonic distortion products. The second term may be ignored if e_3 is small, and this frequently obtains in practice. If not, it represents ten interference bands. The last term gives a pure whistling tone plus fourteen interference bands. As in the general case, the whistling tone is of variable pitch, the variation depending on the accuracy with which the frequency of the local oscillator keeps n radians per second ahead of the signal-frequency circuit. The mutual effect of the signals results in an *increase* in the modulation of the desired signal, for

$$k_2\,\Delta I_A/\Delta e_1 = 4e_1e_2^2 + 4e_1e_3^2 + 8e_1e_2e_3\cos\epsilon t \qquad \text{......(19)},$$

in the presence of e_3, and

$$k_2\,\Delta I_A/\Delta e_1 = 4e_1e_2^2 \qquad \text{......(20)},$$

in the absence of e_3.

x The ratio x of expressions (19) and (20), giving the increase in modulation due to the interfering signal, is given by

$$x = 1 + (e_3^2 + 2e_2e_3\cos\epsilon t)/e_2^2 \qquad \text{......(21)},$$

and if e_3 be small this becomes

$$x = 1 + 2\,(e_3/e_2)\cos\epsilon t \qquad \text{......(22)}.$$

(When $f = 2n$ this value, e_3^2 being neglected, becomes

$$1 + 2\,(e_3/e_1)\cos\epsilon t).$$

In the absence of the desired signal the interfering signal does not contribute to the audio output. There is, of course, an infinity of values which may be accorded to f, and in cases where the interfering signal is due to a powerful local station—that is to say, where e_3^2 is not negligible—each different value of f results in a different audio output and, in general, a different value of x. It would serve no purpose to consider further cases here, but there are certain conclusions which may be drawn from the preceding analysis.

The fact that the number of interference bands in the audio output is greatly reduced when e_3^2 is negligible stresses the importance of careful screening in the pre-first-detector stages. Further, a receiver employing a well-screened stage of radio-frequency amplification is, for the same reason, to be preferred to a receiver in which the first stage is the first detector. The use of band-pass filters and of circuits of low decrement in the signal-input circuit also aids in this direction.

These points are referred to only briefly as it is realized that the principles of superheterodyne-receiver design are now fairly well established, and, further, it would be out of place to discuss them in this paper.

APPENDIX

T_s We have to expand the general term T_s, where $T_s = A_sV^s$, in equation (10), where V has the value given by equation (6) and s is even. Replacing $e_1^2 + e_2^2 + e_3^2$ by $2e^2$ in equation (6) and writing the value of V^2 in full, we have

$$T_s = 2^{\frac{1}{2}s} A_s\,[e^2 + e_1e_2\cos nt + e_1e_3\cos ft + e_2e_3\cos(n-f)\,t]^{\frac{1}{2}s}.$$

Since s is even, $\frac{1}{2}s$ is integral, and expanding T_s by the multinomial expansion we have

$$T_s = 2^{\frac{1}{2}s} A_s \sum_{H,J,K,L=0}^{\frac{1}{2}s} \beta a^H b^J c^K d^L,$$ H, J, K, L

where $\beta = {}_HC_{\frac{1}{2}s} \times {}_JC_{\frac{1}{2}s} \times {}_KC_{\frac{1}{2}s} \times {}_LC_{\frac{1}{2}s};$ β

$$a = e^2; \quad b = e_1e_2 \cos nt; \quad c = e_1e_3 \cos ft; \quad d = e_2e_3 \cos (n-f)\, t;$$ a, b, c, d

and $H + J + K + L = \frac{1}{2}s.$

As we are only concerned with the angular frequencies present in ΣT_s, the values of the coefficients will be ignored. It is clear that T_s is composed of a sum of products of powers of cosines which can be expressed in terms of multiple angles. Replacing the powers of the cosines by the multiple angle series, we see that each term in the summation T_s is itself a summation, and we obtain

$$T_s = 2^{\frac{1}{2}s} A_s \sum_{H,J,K,L=0}^{\frac{1}{2}s} \beta a^H \sum_{j,k,l=0}^{J,K,L} \gamma \cos jnt \,.\, \cos kft \,.\, \cos l(n-f)\, t,$$ j, k, l

where γ depends on the values of j, k, and l. Rewriting this, we have γ

$$T_s = 2^{\frac{1}{2}s} A_s \sum_{H,J,K,L=0}^{\frac{1}{2}s} \beta a^H \sum_{j,k,l=0}^{J,K,L} \gamma' \left[\cos \{(j+l)\, n + (k-l)\, f\}\, t + 3 \text{ similar terms}\right],$$

where γ' takes account of the additional constants introduced by the re-arrangement. In equation (10) we have

$$I = \sum_{s=2}^{\infty} T_s \; (s \text{ even}),$$

whence

$$I = \sum_{s=2}^{\infty} 2^{\frac{1}{2}s} A_s \sum_{H,J,K,L=0}^{\frac{1}{2}s} \beta a^H \sum_{j,k,l=0}^{J,K,L} \gamma' \left[\cos \{(j+l)\, n + (k-l)\, f\}\, t + 3 \text{ similar terms}\right].$$

Giving the successive values to j, k, l, H, J, K, L and to s we see that the angular frequencies of the terms in the summation are exactly contained in the expression $\kappa n \pm \lambda f$, where κ and λ are positive integers. When $\kappa n \pm \lambda f = \pm n \pm \eta$, where $\eta < \epsilon$, a value can be assigned to f, and the terms actually contributing to the output can be picked out, as has been stated in the text. The only values of κ and λ which must be excluded are those given by $\kappa > 1$, $\lambda = 0$, and $\kappa = \lambda = 0$, and hence the array (12) is obtained. λ, κ, η

DISCUSSION

Mr A. Hall. The author mentions only interference due to the presence of incoming stations, but, as has been pointed out by Mr Willans, there can be interference when only one station is being received, the worst offender being the second detector valve. Even the fifth and sixth harmonics of the intermediate frequency originating at the second detector valve can cause serious interference. In one commercial form of superheterodyne receiver I have found an interference which I would like the author to consider. One station was being received, namely, an oscillating wave-meter, the strength of the signal entering the receiver was fairly considerable, and the amplification of the receiver was adjusted to be fairly large by suitable adjustment of grid bias. Then if the receiver was tuned accurately by the wave-meter no interference was received and any modulation could be freely heard. But when the receiver was tuned to a frequency a few thousand cycles higher a serious heterodyne note was heard. This took place over the whole of the wave-band range. If the author can explain this trouble I shall be very thankful.

AUTHOR'S reply. Although in my analysis I set out to consider interference from a source external to the receiver, certain other forms of interference, such as that due to the generation of harmonics by the local-oscillator valve, or to back-coupling between the second and the first detector valves, may be readily taken into account by assigning appropriate values to f. With regard to the problem stated by Mr Hall, the data given are not sufficient to permit of a definite solution. If we put $e_1 = 0$ and $f = -\Delta\omega\ (\Delta\omega < \epsilon)$ we see that the output from the second detector valve contains only the modulation (if any) of the wave-meter signal. It is clear, therefore, that the whistling tone experienced in this case is due to some cause other than that treated in the present paper.

REVIEWS OF BOOKS

Les Bandes Moléculaires dans les Spectres Stellaires, par P. SWINGS. Pp. 29. (*Actualités Scientifiques et Industrielles*, No. 50. Paris: Hermann et C^{ie}, 1932.) 7 francs.

The appearance of this excellent monograph is particularly welcome on account of the difficulty, which many readers experience, in finding the rather widely scattered papers on this important branch of astrophysics. It is a clear, concise and critical survey, such as might be expected of an author who has made a special study of the subject at the Yerkes observatory after carrying out elsewhere some laboratory investigations of certain band-spectra. The bands which have been identified in stellar spectra are all due to neutral diatomic molecules and occur only in the cooler stars (types F, G, K, M, S, R, and N). Amongst these molecules the author includes H_2 without a query or a comment, although some astrophysicists of long experience doubt the reported identity with sun-spot lines of certain H_2 band lines. To the author's list of molecules it seems safe to add SiH, band lines of which have been identified in the sun-spot spectrum. The band head at λ4752 which, together with the one at λ4744 due to $C^{12}C^{13}$, accompanies the strong $C^{12}C^{12}$ Swan band head at λ4737 in certain stars, is attributed on p. 15 to $C^{12}C^{14}$. It should, however, be mentioned that this interpretation of the band has been questioned by Menzel, who attributes it, apparently with greater justification, to $C^{13}C^{13}$, thus removing any evidence there was of a third carbon isotope C^{14}. The booklet closes with a very useful list of references to original papers. It is the second of this admirable series of monographs dealing with the study of molecular bands in spectra of celestial sources, a former one (No. 16, 1929) by F. Baldet having been devoted to comet spectra. W. J.

Structures et Propriétés Optiques des Carbonates, par H. BRASSEUR. Pp. 29. (*Actualités Scientifiques et Industrielles*, No. 51. Paris: Hermann et C^{ie}, 1932.) 7 francs.

This monograph deals chiefly with the refractive indices, birefringences and related properties of carbonates in the two crystalline forms, e.g. of $CaCO_3$ in the well-known forms calcite and aragonite. It also includes a brief account of the same optical properties of certain crystals in which the CO_3 group is replaced by one of the groups BO_3, NO_3, TiO_3. The subject is founded upon some of the researches of W. L. Bragg and later investigations by others, including the author himself, who, as we learn from a preface by V. Henri, has worked upon this subject in W. L. Bragg's laboratory and elsewhere. The four diagrams would gain in usefulness if specific reference were made to them either in captions or in the text itself and if symbols were included in all instead of only one of them. So broad a title seems hardly suitable for a monograph which excludes such important optical properties of these crystals as their infra-red spectra, about which much valuable information has been won by Liebisch and Rubens, by C. Schaefer and his collaborators and by Rawlins, Taylor and Rideal. Within its set limits the booklet is interesting and valuable. W. J.

Acoustics and Architecture, by PAUL E. SABINE. Pp. ix + 327. (McGraw-Hill Publishing Co., Ltd.) 21*s*. net.

The two introductory chapters of this book contain those notions concerning the nature and properties of sound necessary for the appreciation of its principal theme, and justify the author's departure from the more usual title of "Architectural Acoustics" by which works of similar scope are known. In these chapters, which also provide an historical background, the essential preliminaries are disposed of in a simple but businesslike manner and the reader is introduced to the subject of sustained sound in an enclosure by the consideration of stationary and semi-stationary waves in a tube. We note that the diagram illustrating the last named system has the unusual merit of being correctly described and drawn, and, passing to a description of Prof. Wallace Sabine's work on the intensity distribution in a room, we meet one of the characteristic features of the book—the prominence given by the author to the pioneer work of his kinsman and the researches with which he himself has been associated at the Riverbank Laboratories. A description of W. C. Sabine's work may appeal especially to those without easy access to the *Collected Papers*, while an account of the author's work under a single cover and fitting easily into the general ensemble is too welcome to require the apology made in the preface. Reverberation is studied with absorption considered as a continuous and then, in the modern mode, as a discontinuous phenomenon, while the proofs of the corresponding reverberation formulae are based on Buckingham's analysis the kernel of which is given in an appendix. The methods of measuring absorption coefficients at normal and at random incidence having been described and the results considered, there follow two chapters of considerable practical interest. The first of these is concerned with the calculation of the reverberation time of an auditorium and a discussion of the "acceptable range of reverberation times," which expression the author prefers in place of "optimum reverberation time"; while, in the second, salient features of auditorium design are illustrated by architectural drawings of actual buildings. The account of the measurement and control of noise is good and on the subjects of sound-transmission and insulation the author has much to say that is of interest. Particularly valuable is his critical comparison of the methods that have been employed for measuring the transmission of sound by walls and his demonstration from the data obtained that, in general, it is the mass per unit area of the wall which plays the predominating rôle in sound-reduction. In the chapter devoted to machine isolation, oscillograms of machine and floor vibrations are reproduced and serve to illustrate the clear distinction which must be drawn between measures which reduce the vibration of the machine on its supports and those which reduce the transmission of vibration to the supporting structure. The book concludes with a number of appendices containing useful data on absorption coefficients.

This volume has been written by a master of the craft which it describes and, as it continuously reflects the eminently practical outlook of its author, it may be recommended not only to those whose interest is of an academic nature but also to those actively engaged in the design and acoustical correction of buildings. E. J. I.

The Colloid Aspects of Textile Materials and Related Topics. A General Discussion held by the Faraday Society. London, 1933. Pp. 368. Price 15*s*. 6*d*. net.

By a striking coincidence this volume has appeared within a few weeks of the twentieth anniversary of the first general discussion on colloids arranged by the Faraday Society, that held on March 12, 1913, on the viscosity of colloids. Few things could more vividly impress a reader with the astonishing development of the discipline than a comparison of the two reports. Twenty years ago investigators were concerned much more in discovering strange and anomalous properties of colloidal solutions, and in developing a classification and nomenclature, than in attempting to discover why a number of substances of the highest importance exhibited colloidal behaviour. It is on the latter problem that recent research on cellulose and proteins has concentrated, and it has achieved an astonishing measure of success by bringing into action the whole armoury of modern experimental methods. Measurements of the elastic and optical properties of natural and artificial cellulose fibres, X-ray analysis, viscosity measurements and determinations of the osmotic pressure of sols of cellulose esters, as well as the exhaustive application of classical chemical methods like methylation, have produced results which dovetail very satisfactorily. The structure of the cellulose fibre deduced from an imposing mass of concordant evidence is described as follows by Prof. H. Mark in his opening paper: "Cellulose...consists of fibres with a diameter between 1 and 5 deniers or 80 and 400μ, which have often a very irregular shape. These fibres are built up from the so-called *cellulose micelles*. They are bundles of long molecular chains which are held closely together. We do not know exactly how many of these chains form one micelle, and it seems to depend to a very great extent upon the treatment which the sample has undergone, but we may estimate that one of these packets in native cotton or ramie fibres consists of about 40 or 60 of these chains. We have reason to believe that the single chains of one special sheaf are not all exactly of the same length and structure; it seems, however, that the differences are not very great, so that we are entitled to speak of a certain *average length* and structure of these chains. The diameter of a micelle is between 50 and 70 Å., so that one single fibre contains about ten million micelles in its cross section.

"The chains themselves are built up of glucose units linked together by consecutive 1-4-glucosidic bonds; they are called *main valence* chains and form the very backbone of the whole structure; their average length is not yet quite fixed but, it seems, one may assume for the most carefully treated natural samples that the chains contain about 150 or 200 glucose molecules, and that this number decreases very rapidly with every chemical treatment of the fibre. Glucose units, main valence chains and micelles are the three essential building stones of cellulose fibres."

The next problem of fundamental interest to the colloid physicists is: into what elements is this astonishing structure broken up when cellulose, or one of its esters, goes into solution? The answer "The micelle!" would have been unanimous a few years ago and would still be that given by a considerable number now, there being some diversity of opinion regarding the mechanism by which the high viscosity so characteristic of these sols was brought about. In recent years however Prof. Staudinger, who gives a comprehensive summary of his work, has been led to a different view, in the first instance by studying substances of high molecular weight which could be obtained in the laboratory by polymerization of comparatively simple bodies, e.g. polyoxymethylenes and polystyrenes. The chemical investigation of these bodies, and later of natural substances of high molecular weight like rubber and cellulose, "arrived at the result that these substances consist of very long molecules, in which a hundred or more single molecules are bound by means of main valencies into chains, and it was further proved that these molecules, which were termed fibre molecules (*Fadenmoleküle*), dissolve normally, like the molecules of substances of low molecular weight....The properties of their solutions can, therefore, not result from a micellar structure of the colloid particles and special solvation phenomena occurring with them, but the colloidal nature of the solutions is connected with the size and special shape of the molecules. The investigation of this connection and the results of viscosity experiments provided confirmation for the results found chemically."

A brief summary only of Prof. Staudinger's results can be given here. He calls *specific viscosity* the increase in viscosity produced by the dissolved substance, i.e. if η_r is the relative viscosity $\eta^{\text{solution}}/\eta^{\text{solvent}}$, then $\eta_{sp} = \eta_r \sim 1$. For long molecules he then finds

$$\eta_{sp}/c = K_m M,$$

where M is the molecule weight, K_m a constant for the particular homologous series, and c "the concentration of a primary molar solution," which quantity is defined as follows: "By the primary molecule of a long chain molecule is here designated that structural unit which, when regularly linked end to end, builds up the long chain molecule. The primary molecule of the normal paraffins and paraffin derivatives is the CH_2 group; a primary molar solution of such substances has, therefore, a concentration of 1·4 per cent." Since this quantity is also a constant for a given series, the formula states that, other things being equal, the specific viscosity is proportional to the molecular weight or the chain length. Prof. Staudinger assumes the molecules to be straight and to make "elastic oscillations like a glass fibre," but not to be flexible like say a silk filament. The effect of these oscillations is that the molecules have a "sphere of activity" which, *for purposes of calculation* (his italics), he takes to be a flat cylinder with the length of the chain as diameter and its diameter as height. Only solutions of such low concentration that the aggregate volume of these cylinders is smaller than the total volume of solution are suitable for the determination of molecular weights.

The somewhat arbitrary hydrodynamics does not seem to have troubled the meeting as much as the concept of straight molecules, which seems to have been unacceptable especially to the investigators of surface films, like Rideal, Adam and Katz. The question whether viscosity measurements can be utilized to determine molecular weights was, however, raised in a much more acute form by the results submitted by Prof. E. H. Buchner (with P. J. P. Samwel). The investigators had measured, by a new and ingenious method, what is undoubtedly the true osmotic pressure of cellulose acetate solutions in various solvents, and found mean values of 34,300 to 41,000 for different samples, which are in good agreement with those obtained by other methods. The specific viscosity of solutions of equal concentrations should therefore, according to Staudinger, be approximately the same, but actually it varies from 1·28 to 4·01. Incidentally the specific viscosity decreases rapidly with rising temperature which, needless to say, does not affect the molecular weight. The discussion did nothing to clear up this discrepancy. It may also be useful to point out that, in the absence of other evidence, osmotic-pressure measurements cannot distinguish between micelles and macromolecules; in fact, the emphatic distinction between the two may remind critical readers of a well-known epigram by Swift.

The fibres of animal origin, which consist of proteins, have been studied as far as their insolubility permits by the same methods as the cellulose fibres, and here again X-ray examination has confirmed and completed the picture first sketched by the chemist. Drs Dorothy Jordan Lloyd and Henry Phillips, acknowledging an earlier summary by Astbury, describe it as follows: "Silk, stretched hair or wool and collagen fibres have been shown to be built up of long chain molecules lying parallel to the fibre axis. The long molecules consist of a repeating unit, of which three atoms lie on the spiral or zig-zag axis of the molecule, while the remainder form lateral extensions—the whole being a long polypeptide chain with the length of the repeating unit 3·5 Å." How these structural units are combined in natural fibres, and how the mechanical properties depend on the configuration of these elements and on their grouping in the fibre, are questions which are dealt with in a number of fascinating papers. It is difficult to choose a single example, but perhaps the paper by Dr S. G. Barker on "The physical significance of crimp or waviness in the wool fibre" will serve as well as any to illustrate the intricacies of a single problem, and the great number of possible methods of attack from the physical side alone, which have to be supplemented by physiological and biochemical investigation on secretion and growth. Some of the relations found are surprisingly—and misleadingly—simple. Thus, if the true area of the cross section, which is elliptical, is taken into account, the product (area × number of crimps per inch) is reasonably constant. In view of this result, research for some time was concerned chiefly with the number of waves per unit length of fibre, until further work showed that this figure was not really significant, but that "the total number of crimps per fibre along its entire length" was constant for a given fleece. "In many locks the mean total number of crimps in each fibre was the same irrespective of the length of the fibre" although the difference between the length of the shortest and longest fibre amounted to as much as 9 cm.

The geometrical form of the crimp may be anything from a plane sine curve to a helix, with a number of intermediate types: thus the sine curve may not throughout its length lie in one plane, but in a succession of planes inclined to each other. Similarly the helix may have a pitch which varies or even changes sign, i.e. a right-handed helix may become left-handed and *vice versa*. A mathematical expression covering all these types has been formulated by Tunstall.

These regularities having been established by observation, there remains the formidable task of discovering the mechanism producing them. As with other structures of organic origin "models" can be produced by comparatively simple physical methods which can bear no real resemblance to what goes on in the organism: an oscillating jet of gelatin sol discharged into a dehydrating liquid sets to a filament which, after drying, closely resembles a wool fibre. Although surface tension effects and dehydration may be operative in the latter too, their action is spread over a very considerable period, and ancillary hypotheses postulating periodicity in the physiological activities of the secreting organ, the follicle, become necessary.

These, and much else contained in the volume under review, is outside the province of the physicist. But there is also much which will afford him the satisfaction of knowing that, in the comparatively short time during which the physicist has been called upon to assist in the study of textile fibres, he has certainly magnified his office. E. H.

Lehrbuch der Glasbläserei, by CARL WOYTACEK. Technisch-Gewerbliche Bücher, Band 7. Pp. vii + 319. (Wien: Julius Springer.) Price RM. 22.50.

A good book on glass-blowing can be of great value to the research worker and laboratory assistant as well as to the professional glass-blower, and the above volume is one that can be recommended to all who are interested in the subject. The treatment is considerably more detailed and comprehensive than that found in the majority of books, and the portions dealing with glass-blowing proper are written with the clear style of the expert who knows precisely how to present his subject. The volume is divided into two sections, the first being a general introduction while in the second the manufacture of special apparatus is dealt with. At the beginning of part 1 a survey is made of the grades of glass in common use, and the selection of blowpipes, glass tools, blowers and similar apparatus. The author passes to the correct method of holding the glass tubing so that it can be rotated steadily in the flame. Instructions are given for drawing a capillary and a series of graded exercises lead to the more complicated work such as the manufacture of taps. This section of the book is admirable; every requisite detail is given and, when necessary, illustrated. The diagrams are a noteworthy feature; they are numerous and indicate clearly what is required at each stage of the work. The only limitation is that the book is written for continental workers and may require a little adaptation when applied to English conditions. There is, for example, no mention of pyrex glass and the type of flame best suited for working it. Probably the majority of readers would also have welcomed a chapter on the working of fused quartz in the blowpipe.

Instructions are given in the second section regarding the manufacture of all kinds of specialized apparatus—thermometers, barometers, standard volumetric and gas-analysis glassware, vacuum pumps, discharge tubes and mercury-vapour lamps. An immense amount of information is thus collected together, but it is doubtful whether all of it strictly belongs to a book on glass-blowing. For example, the description of Geryk, Gaede, and similar oil pumps could have been omitted and a reference to a suitable volume on vacuum practice given. A difficulty that arises in some of the specialized branches is that, as the author admits, the assistance of an expert is required to obtain a working knowledge of the process. With such help detailed written instructions seem unnecessary, and without it they are not of very much use. On the other hand there are few who will not find much information that is useful in this section, and the book as a whole is the best work on glass-blowing that the reviewer has had the pleasure of reading. K. H. P.

Heat, Light, and Sound, by E. NIGHTINGALE. Pp. xii + 378, with 11 plates and 363 figures. (London, G. Bell and Sons, Ltd., 1931.) 6*s*. 6*d*.

The writer of an elementary text-book of physics must necessarily travel a well-worn path. The author of this book, therefore, has contented himself with a ready-mapped route, and with few exceptions has followed the conventional order of treatment. None the less, new departures in two directions may be noted. Firstly a wider cultural value is given to formal observations and records, by the skilful insertion of historical accounts. In this way the beginner, for whom this book is written, is pleasantly introduced to the first principles and to their origins at the same time. Secondly, the text, broken up by many new and redrawn illustrations and diagrams, bears a fresh and interesting appearance. In a few places a certain laxity of description and explanation may be observed, as in the account of the joining of two ice blocks by pressure, p. 82; the statement that the blocks will stick together even under warm water hardly elucidates. The diffusion of air and hydrogen in wide jars does not immediately prove that "the molecules are in rapid motion" (p. 94). Such minor criticisms may be made, but these smaller faults do not obscure the outstanding attractiveness of the volume for both teacher and student, to whom it may be recommended with confidence. J. P. A.

Experimental Hydrostatics and Mechanics, by E. NIGHTINGALE. Pp. x + 244, with 20 illustrations and 182 text figures. (London, G. Bell and Sons, Ltd., 1931.) 4*s*. 6*d*.

In this little book the methods successfully employed in *Heat, Light, and Sound* are developed in a more pronounced degree. Anyone whose youth was marred by the study of mechanics of the purely algebraic kind, with academic problems to be solved by formula at the end of each section, will desire to have this book, although it is meant for beginners. It is true that if in a critical mood he will find rather trying the frequently repeated qualifications "great," "remarkable," "famous," as applied to well-known investigators and experiments, but he is not a schoolboy. The historical developments are carefully described with new and interesting illustrations. After a general historical introduction, the book sets off with the principle of moments, centres of gravity, and equilibrium, employing a rough and ready definition of force. Hydrostatics follows. Then, after a more detailed study of force and equilibrium and the conceptions of work and power, dynamics and the laws of motion finish the book. This order, to which grave objection might be raised on logical grounds, is deliberately chosen as more suited to the beginner. While one may doubt the wisdom of this decision, there is no question that the author has revitalized the presentation of elementary mechanics. No teacher of the subject would be wise to neglect this book. J. P. A.

Elementary Hyperbolics, by M. E. J. GHEURY DE BRAY. Vol. 1, pp. xi + 351. Vol. 2, pp. xii + 209. (London: Crosby, Lockwood and Son, 1931.)

The book is specially adapted to the requirements of beginners and is intended for those technical students who do not take easily to mathematics. Provided they are sufficiently tenacious of purpose such students will find every step filled in, so that they can hardly be "stumped" in reading the book, though they will need all their wits about them if they are to retain the thread of an argument which extends over perhaps three pages of algebra.

If they are the sort of people who are helped by speaking of: "How we descend a flight of steps, and where they lead us" instead of "How to evaluate a continued fraction," then this book will certainly help them.

The reviewer feels that much of the difficulty of the hyperbolic functions would be removed if the hyperbola were not introduced. The difficulty as to the unit of measurement for the argument could not then arise, and much tedious algebra would be avoided.

What will be the reaction of the technical student to the assertion on p. 108 that if $2u = 2\theta$, then u is not equal to θ, we do not know. His shock will be no less severe than that of the mathematician who on another page is supposed to be horrified at the suggestion that $\cosh(\mathrm{dog}) = \frac{1}{2}(e^{\mathrm{dog}} + e^{-\mathrm{dog}})$. Actually his surprise might be so small that he would even be prepared to admit that $\cosh x = \frac{1}{2}(e^x + e^{-x})$ even when $x =$ (the numerical value of) Gheury de Bray!

The second volume is devoted to the application of vectors and of hyperbolic functions to the solution of mechanical and electrical problems, and can be particularly warmly commended.

J. H. A.

Tables for the Development of the Disturbing Function with Schedules for Harmonic Analysis, by Ernest W. Brown and Dick Brouwer. Pp. 85. (Cambridge: University Press, 1933.) 10*s*. 6*d*.

The disturbing function R is such that dR/ds gives the disturbing force on one planet, in the direction s, due to another planet. When there are several disturbing bodies, R is the sum of a number of functions each of the form $m/\rho - mr \cos \omega/r'^2$ where m is the mass of the disturbing body, ρ the distance between the two, r, r' the distances of the disturbed and disturbing bodies from the sun and ω the angle between r and r'.

The numerical treatment of the function is facilitated by the expansion of

$$(1 - 2\alpha \cos S + \alpha^2)^{-n}$$

in the form

$$(1 - \alpha^2)^{-n} (A_n + B_n' \alpha \cos S + B_n'' \alpha^2 \cos 2 S + B_n''' \alpha^3 \cos 3 S + \ldots),$$

the coefficients A and the first eleven of the coefficients B being given in this table for values $-\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}$ and $-\frac{7}{2}$ of $-n$. Actually the quantities tabulated are the logarithms to 7 figures of A and B for values of $\alpha^2/(1 - \alpha^2)$ from 0 to 2·50, proceeding by steps of 0·01. Natural values would be less useful even when a calculating machine is available, since products of several factors would normally be required.

We may note that the extraction of the factor $(1 - \alpha^2)^{-n}$ simplifies the numerical work but not the analytic nature of the Bs which are quite closely related to ordinary Legendre functions if the expansion is made simply in powers of α.

The rest of the book contains other tables of use in precise calculation of orbits, the only other one likely to be of interest to the general physicist being the expansion of $(1 - 2\alpha \cos S + \alpha^2)^{-n}$ in the form $(1 - \alpha^2)^{-n-\frac{1}{2}} (C + D_n' \cos S + D_n'' \cos 2 S + \ldots)$ for $n = + \frac{1}{2}$ and $+ \frac{3}{2}$. This time, the natural values to 5 figures are entered as functions of α itself, which proceeds from 0·900 to 0·950 by steps of 0·001.

The book is stated to be the same as part 5 of volume **6** of the *Transactions of Yale University Observatory*, and it has apparently been printed from the same plates, since the page numbers commence at 73.

J. H. A.

THE PROCEEDINGS OF THE PHYSICAL SOCIETY

VOL. 45, PART 5 *September* 1, 1933 NO. 250

535.338:546.48

HYPERFINE STRUCTURE IN THE SPARK SPECTRUM OF CADMIUM

E. GWYNNE JONES, Beit Scientific Research Fellow, Imperial College of Science and Technology, London

ERRATA

In the *Proceedings of the Physical Society*, Volume 45, Part 4, "Interference tones in superheterodyne receivers," by W. F. Floyd, B.Sc., page 610.

For 621.396:621.54 *read* 621.396.621.54.

"A method of measuring the specific heats of poor conductors," by W. G. Marley, M.Sc., page 591.

For 536 63:536.62 *read* 536.63 536.62.

possess satellites. The structures of these lines were accurately measured and explained by Schüler and Keyston*, who assigned the nuclear moments $I = 0$ to the even isotopes (mass numbers 110, 112, 114 and 116) and $I = \frac{1}{2}$ to the odd isotopes (111 and 113). The present investigation was carried out in order to examine the lines of Cd II that fall in the region λλ 4200–8500, where a silvered interferometer can be used to best advantage.

§ 2. EXPERIMENTAL RESULTS

The spectrum, which had already been analysed by von Salis† was excited in a Schülerlamp of the hot cathode type‡, in which the required lines were very intense. Fourteen lines (involving thirteen terms) were examined; the twelve lines in table 1 were found to have no structures.

Table 1. Cd II lines which have no structures

λ	Classification	λ	Classification	λ	Classification
4285	$8\,^2S_{\frac{1}{2}}-6\,^2P_{\frac{1}{2}}$	6759	$6\,^2P_{\frac{3}{2}}-6\,^2D_{\frac{3}{2}}$	7237	$6\,^2D_{\frac{3}{2}}-6\,^2F_{\frac{5}{2}}$
4412	$8\,^2S_{\frac{1}{2}}-6\,^2P_{\frac{3}{2}}$	5337	$5\,^2D_{\frac{3}{2}}-4\,^2F_{\frac{5}{2}}$	7284	$6\,^2D_{\frac{5}{2}}-6\,^2F_{\frac{7}{2}}$
6465	$6\,^2P_{\frac{1}{2}}-6\,^2D_{\frac{3}{2}}$	5378	$5\,^2D_{\frac{5}{2}}-4\,^2F_{\frac{7}{2}}$	6355	$4\,^2F_{\frac{5}{2}}-5\,^2G$
6726	$6\,^2P_{\frac{3}{2}}-6\,^2D_{\frac{5}{2}}$	5381	$5\,^2D_{\frac{5}{2}}-4\,^2F_{\frac{5}{2}}$	6360	$4\,^2F_{\frac{7}{2}}-5\,^2G$

---

* H. Schüler and J. E. Keyston, *Z. f. Phys.* **67**, 433 (1931).

† G. von Salis, *Ann. d. Phys.* **76**, 145 (1925).

‡ H. Schüler, *Z. f. Phys.* **35**, 323 (1926).

AB
with
Fro
is –

I
the
poss
expl
the
isot
exan
inte

Sch
inte
in ta

PI

THE PROCEEDINGS OF
THE PHYSICAL SOCIETY

VOL. 45, PART 5 September 1, 1933 No. 250

535.338:546.48

HYPERFINE STRUCTURE IN THE SPARK SPECTRUM OF CADMIUM

E. GWYNNE JONES, Beit Scientific Research Fellow, Imperial College of Science and Technology, London

Communicated by Prof. A. Fowler, F.R.S., June 15, 1933. *Read July* 7, 1933

ABSTRACT. The Cd II spectrum has been investigated in the region λλ 4200–8500 with Fabry-Perot etalons. Of the thirteen lines examined, only λ 8067 has any structure. From the structure of the $6\,^2S_{\frac{1}{2}}$ term it is calculated that the g (I) factor of the odd isotopes is −1·25 proton magnetons.

§ 1. INTRODUCTION

In the spectra of cadmium, only four arc lines have been thoroughly investigated for hyperfine structure. Michelson proposed λ 6438 ($5\,^1P_1$–$6\,^1D_2$) as the standard of wave-length measurements on account of its lack of structure, and the visible triplet λλ 4678, 4800 and 5086 ($5\,^3P_{0,1,2}$–$6\,^3S_1$) has long been known to possess satellites. The structures of these lines were accurately measured and explained by Schüler and Keyston*, who assigned the nuclear moments $I = 0$ to the even isotopes (mass numbers 110, 112, 114 and 116) and $I = \frac{1}{2}$ to the odd isotopes (111 and 113). The present investigation was carried out in order to examine the lines of Cd II that fall in the region λλ 4200–8500, where a silvered interferometer can be used to best advantage.

§ 2. EXPERIMENTAL RESULTS

The spectrum, which had already been analysed by von Salis† was excited in a Schülerlamp of the hot cathode type‡, in which the required lines were very intense. Fourteen lines (involving thirteen terms) were examined; the twelve lines in table 1 were found to have no structures.

Table 1. Cd II lines which have no structures

λ	Classification	λ	Classification	λ	Classification
4285	$8\,^2S_{\frac{1}{2}}$–$6\,^2P_{\frac{1}{2}}$	6759	$6\,^2P_{\frac{3}{2}}$–$6\,^2D_{\frac{3}{2}}$	7237	$6\,^2D_{\frac{3}{2}}$–$6\,^2F_{\frac{5}{2}}$
4412	$8\,^2S_{\frac{1}{2}}$–$6\,^2P_{\frac{3}{2}}$	5337	$5\,^2D_{\frac{3}{2}}$–$4\,^2F_{\frac{5}{2}}$	7284	$6\,^2D_{\frac{5}{2}}$–$6\,^2F_{\frac{7}{2}}$
6465	$6\,^2P_{\frac{1}{2}}$–$6\,^2D_{\frac{3}{2}}$	5378	$5\,^2D_{\frac{5}{2}}$–$4\,^2F_{\frac{7}{2}}$	6355	$4\,^2F_{\frac{5}{2}}$–$5\,^2G$
6726	$6\,^2P_{\frac{3}{2}}$–$6\,^2D_{\frac{5}{2}}$	5381	$5\,^2D_{\frac{5}{2}}$–$4\,^2F_{\frac{5}{2}}$	6360	$4\,^2F_{\frac{7}{2}}$–$5\,^2G$

---

* H. Schüler and J. E. Keyston, *Z. f. Phys*. **67**, 433 (1931).

† G. von Salis, *Ann. d. Phys*. **76**, 145 (1925).

‡ H. Schüler, *Z. f. Phys*. **35**, 323 (1926).

The line λ 8067 ($6\,^2S_{\frac{1}{2}}$–$6\,^2P_{\frac{3}{2}}$) has a small structure comprising three components, an intense line (due to the unresolved even isotopes) bracketed by a much fainter doublet (with a separation $\delta\nu$ of 0·11 cm.$^{-1}$) which is ascribed to the odd isotopes. Since the absence of hyperfine structure in λ 6726 and λ 6759 proves that the level $6\,^2P_{\frac{3}{2}}$ is single, the measured structure in λ 8067 is that of the level $6\,^2S_{\frac{1}{2}}$. The intensity ratio and position of the faint doublet indicate that the odd isotopes have nuclear moments I equal to $\frac{1}{2}$ and that the hyperfine levels are inverted, in complete agreement with the analysis of Schüler and Keyston* for the visible triplet of Cd I. The related line λ 8530 ($6\,^2S_{\frac{1}{2}}$–$6\,^2P_{\frac{1}{2}}$), which is, however, too faint to be analysed completely, shows indications of the same structure as that obtained for λ 8067.

A number of new Cd II lines have been observed in the far red, and it has been found possible to classify three of these, namely

λ 8530·3	$6\,^2S_{\frac{1}{2}}$–$6\,^2P_{\frac{1}{2}}$
λ 8389·3	$7\,^2S_{\frac{1}{2}}$–$6\,^2P_{\frac{3}{2}}$
λ 7940·8	$7\,^2S_{\frac{1}{2}}$–$6\,^2P_{\frac{1}{2}}$.

The new doublet involving the $7\,^2S_{\frac{1}{2}}$ term, which had previously only been estimated from combinations in the extreme ultra-violet, fixes its value as 29,075·5 cm.$^{-1}$ These new lines were all too faint to be photographed successfully through the interferometer.

§ 3. DISCUSSION OF RESULTS

The measurement of a hyperfine separation in a ^2S-term of the odd isotopes renders possible a calculation of the magnetic moments associated with the nuclear spins.

a

It has recently been shown† that, for penetrating *s* electrons, the interval factor *a* may be expressed by the formula

$$a=\frac{8R\alpha^2 Z_i Z_0^2\,\kappa\left(\tfrac{1}{2};\,Z_i\right)}{3\,n_0^3}\cdot\frac{g\,(I)}{1838}\qquad\ldots\ldots(1),$$

R, α, n_0 — Z_0, Z_i — κ — *g* (*I*)

where R, α, n_0 are respectively Rydberg's constant, Sommerfeld's fine-structure constant, and the effective principal quantum number of the spectral term under consideration. Z_0 and Z_i are the effective nuclear charges experienced by the electron in the outer and inner parts, respectively, of the penetrating orbit. The function κ represents a relativity correction. On substitution of the appropriate numerical values (1) the $g\,(I)$ factor (the ratio of magnetic to mechanical moments) for the nuclei of the odd isotopes is found to be − 1·25 proton units. This is in very good agreement with the value − 1·33 calculated by Goudsmit‡ from the measurements§ on certain Cd I lines.

§ 4. ACKNOWLEDGMENT

The author wishes to express his thanks to Prof. A. Fowler, F.R.S., in whose laboratories the work was carried out, for his encouragement and help.

---

* *Loc. cit.* (1) $a=0{\cdot}11$, $n_0=2{\cdot}865$, $Z_0=2$, $Z_i=48$ and $\kappa=1{\cdot}28$.

† S. Goudsmit, *Phys. Rev.* **43**, 636 (1933).

‡ *Loc. cit.*

§ Schüler and Keyston, *loc. cit.*

535.338:546.27

THE INTENSITIES OF BANDS IN THE SPECTRUM OF BORON MONOXIDE

By A. ELLIOTT, Ph.D., D.Sc., Physics Department,
the University, Sheffield

Communicated by S. R. Milner, F.R.S., May 24, 1933.
Read July 7, 1933

ABSTRACT. The intensities of the α bands of BO have been measured by means of an arrangement which gives the intensity of a whole band. Precautions for the detection of systematic errors are described, and the probable error is estimated at about ± 5 per cent. The observed intensities have been compared with theoretical ones calculated from wave mechanics. Morse's wave function is found to give much better results than the harmonic wave function, but shows some discrepancy from theory for higher vibrational states. The theory using the harmonic wave function has been applied to some previous results for the intensities of the β bands of BO. Fair agreement is found for the most part, but a few bands show discrepancies greater than the experimental error. The intensity ratio of the $B^{11}O$ and $B^{10}O$ bands has been measured for two of the α bands. The result, 3·5:1, is in satisfactory agreement with a previous determination of the isotope intensity ratio in the β bands of BO, 3·66:1.

§ 1. INTRODUCTION

The probability that a transition will occur between two vibrational states of a molecule can be calculated by wave mechanics, provided that the molecular constants have been determined with sufficient accuracy. Such calculations have been carried out by Hutchisson (1, 2) and by Price (3). The accuracy of the calculated values depends on the accuracy of the simplifying assumptions which have to be made, and chiefly on the way in which the nuclear potential energy is assumed to depend on the internuclear distance.

As the experimental data available for testing these calculations are rather meagre, it seemed desirable to determine the intensities of a number of bands with as great an accuracy as possible. For such a purpose it is necessary that the bands measured should lie in a region for which accurately calibrated standard lamps are available, and that they should form a system in which overlapping of bands does not occur to a great extent. The α system of boron monoxide in the visible region seemed fairly suitable for the purpose, and was accordingly chosen. It is the object of this paper to describe the determination of the intensities of these bands, and to compare them with the theoretical intensities. The notation used here is that given by Jevons (5).

§ 2. EXPERIMENTAL

The method employed for the determination of relative intensities over a wide range of wave-lengths was substantially the same as that developed by Ornstein and his colleagues at Utrecht (6, 7), with the important addition that an arrangement recently described by Thompson (8) was employed in making the microphotometer record of the bands whose intensities were to be compared. This modification gives a record in which the ordinates are proportional not to plate density but to intensity multiplied by a factor which is constant over a range of about 50 Å., i.e. over a complete band. The record is planimetered to give the area for a complete band. This, when multiplied by the appropriate factor, is a measure of the energy radiated as a result of the vibrational transition in question. Density marks were obtained by photographing the spectrum of a standard lamp through a step slit (9, 10) placed over the spectrograph slit, which was opened wide.

Calibration of standard lamps. Tungsten spiral-filament lamps, run at constant current from accumulators, were used; the colour temperatures of the lamps were determined by different methods. The first lamp used (6 V., 36 W.) had been calibrated at the Physical Laboratory of the University of Utrecht by means of an optical pyrometer (11) and was kindly given to the author by Prof. Ornstein. This lamp was used in method (*a*) to be described later. The lamp used in method (*b*) (12 V., 24 W., Siemens motor-headlight lamp) was calibrated in this laboratory by concentrating its radiation on the slit of a monochromator and observing the galvanometer deflections produced by a thermopile at two suitable wave-lengths (λλ 6563 and 5016). The ratio of these two deflections, after correction for the stray radiation scattered by the optical parts of the monochromator and for the different transmissive powers of this instrument at the two wave-lengths, enabled the colour temperature of the lamp to be calculated from Wien's law. A knowledge of the dispersion of the monochromator at each wave-length is also necessary for this calculation.

Stray light could have been eliminated by using a double monochromator, but as this was not available, screens transparent to the stray radiation (chiefly near infra-red) but opaque to the radiation which is to be measured were used as shutters (12). The difference between the galvanometer deflections with and without these shutters gives the deflection due to the radiation which is to be measured, provided that the shutter transmits all of the stray radiation. As shutters, the Ilford infra-red filter was used when measuring the radiation at λ 6563, and cellophane stained with commercial red ink for λ 5016. These screens transmitted only about 90 per cent of the stray radiation, and in consequence the difference of deflections with and without the shutter was larger than the deflection due to the radiation to be measured. At λ 6563 the percentage of stray radiation was so small as to render further correction unnecessary, but this was not the case at λ 5016. By observing the difference between the deflections obtained at this wave-length with a totally opaque shutter and with the red cellophane screen, the deflection due to the stray radiation transmitted by the screen was found. In similar fashion the deflections due to the stray radiation transmitted by two, three and four thicknesses of the same screen were found. By plotting these deflections against the thickness of screen used and then extrapolating to zero thickness, the deflection due to the stray radiation as it would have appeared with a screen transmitting 100 per cent was obtained. This result, together with the difference between the deflections with and without the single thickness of screen, enabled the deflection due to the radiation of wave-length λ 5016 to be calculated.

The quantity

$$\frac{\left\{\begin{matrix}\text{(fraction of incident light transmitted by the}\\ \text{monochromator and condensing lens for } \lambda\,5016)\end{matrix}\right\}}{\text{(fraction transmitted for } \lambda\,6563)},$$

which may be referred to as the *relative transmission* for these wave-lengths, was determined in the following manner. The monochromator, lamp and condensing-lens were arranged in front of the slit of a spectrograph so that, when the thermopile was removed, the light in the region λ 5016 transmitted by the monochromator fell on the spectrograph slit. The monochromator was sufficiently far from the spectrograph to ensure that only the central part of the spectrograph prism was illuminated. The spectrograph was provided with a step slit. Density marks were photographed with this arrangement; then the monochromator was set to give the region λ 6563 and density marks at this wave-length were taken. The lamp was then placed between the monochromator and spectrograph slit, and density marks were again taken. The current through the lamp was of course kept constant, and all exposure times were the same. After the plate had been photometered in the ordinary way, the relative transmission for the two wave-lengths could be calculated. The method is an adaptation of that devised by Ornstein for the photographic method of calibrating standard lamps(7).

The relative transmission of the monochromator is constant for two given wave-lengths, and hence has only to be measured once. When this determination has been carried out, it is a fairly simple matter to calibrate a lamp by observing the deflections due to the thermopile for two wave-lengths as described above, correcting them for the relative transmission and finally calculating the colour temperature of the lamp from Wien's law. The probable error in the determination of the ratio $E_{\lambda 5016} : E_{\lambda 6563}$ is about ± 1 per cent, giving a probable error of ± 10° in a colour temperature of 2930° K.

E_λ

Intensity-measurements. The spectrum of boron monoxide was excited by allowing the vapour of boron trichloride to pass into streaming active nitrogen containing the necessary trace of oxygen(13, 14). It is of importance in heterochromatic photometry that the exposure times be the same for density marks and for the spectrum in which the intensities are to be measured. Since the energy radiated by the standard lamp is very different for regions of different wave-length, some arrangement is necessary whereby a series of sets of density marks of varying intensity but constant exposure time may be made. Two methods were used.

Method (*a*). A single-prism Littrow spectrograph with glass optical system giving the whole of the visible spectrum on a 10-in. plate was employed for the measurement by this method. In this case the light from the standard lamp passed through the afterglow tube before falling on the spectrograph slit. The condensing lens, used to throw an image of the tube on to the slit, was removed when density marks were being taken. Several sets of density marks were taken with different lamp currents in order to get suitable densities over the wave-length range 4000 to 6000 Å.

When exposure for the BO bands and development had been completed the density marks were photometered at the wave-length corresponding to the most intense part of each band. Where the densities were suitable, two sets of density marks were photometered at the same wave-length so as to enable the relative intensities of the various sets, taken with different currents, to be determined at selected wave-lengths. The relative intensities at the same wave-lengths were then calculated from the colour temperature of the lamp filament, the filament being assumed to behave as a black body at a temperature equal to the colour temperature. The calculated relative intensities differ slightly from those determined experimentally as described above, because the colour emissivity of tungsten$^{(15)}$ is a function of the colour temperature. Correction factors could now be evaluated by which the energy functions E_λ calculated from the colour temperatures could be multiplied. The corrected values E_λ' when multiplied by $d\lambda/ds$ (where s is the distance along the photographic plate) and slit-width w give the correct relative intensities of the light causing the density marks, even though different currents were used. Templates for the modified microphotometer were drawn with a needle point on smoked glass for each band. The ordinates were the degrees of blackening of the density marks and the abscissae were the widths w of the corresponding steps. The bands were photometered with the templates$^{(8)}$, and registrations whose ordinates were proportional to w and abscissae to s were obtained. The constants of proportionality depend only on the dimensions of the microphotometer, and similar factors, and are hence the same for all bands.

E_λ', s
w

The intensity of any part of a band is proportional to the ordinate on the registration at that point multiplied by $E_\lambda' \,.\, d\lambda/ds$. The relative intensity of the whole band is given by multiplying the area under the registration by $E_\lambda' \,.\, d\lambda/ds$. The relative intensities of thirteen bands were determined in this way from photographs taken on Ilford Special Rapid Panchromatic plates. The combined intensity due to $B^{11}O$ and $B^{10}O$ was measured in each case.

Method (*b*). The use of different lamp currents in order to secure suitable density marks over a wide range of wave-lengths leads to a rather complicated procedure for obtaining the values of E_λ', with the introduction of new errors of measurement at each step. In the method now to be described the lamp current remained constant. A magnesium-oxide screen was placed between the afterglow tube and condensing lens when density marks were to be taken; the plane of the screen was at about 45° to the axis of the condensing lens, which remained in position throughout. The standard lamp was placed so that its light fell normally on the white screen, whence it was diffusely reflected into the spectrograph. The intensity of illumination of the screen was altered by altering the distance d between

d

lamp and screen and was calculated from the inverse square law. This could be applied provided d was greater than 20 cm.; the limit is set by the dimensions of the filament and the accuracy sought, the error being 1 per cent.

The intensity of the light causing a density mark was now proportional to $E_\lambda(d\lambda/ds).(w/d^2)$ and was readily calculated. The arrangement had the further advantage that the whole of the prism could be utilized, provided that a large enough white surface was employed. This ensures that the path of the rays is the same for the light giving the density marks and that of the BO bands. The BO bands were photographed and the relative intensities were measured, the above method being used for taking density marks. The further procedure was the same as in method (*a*). In both methods it was necessary to take two photographs of the BO bands, one with a wide and the other with a narrow spectrograph slit, because of the great range of density which occurs on a single exposure. The correlation between the two sets was made from measurements on bands of medium density which were measurable on each plate. A Hilger E 2 quartz spectrograph was employed for the measurements made by method (*b*).

§ 3. COMPARISON OF RESULTS

The relative intensities of the BO bands measured by both methods are given in table 1, where columns (*a*) and (*b*) give the results from plates in which methods (*a*) and (*b*) respectively have been used.

In method (*a*) a standard lamp calibrated by means of an optical pyrometer was used, whereas in method (*b*) the lamp was calibrated by the thermopile method. Different step slits and spectrographs were employed, and the dispersion and prism absorption was widely different in the two cases. The ratio (*b*)/(*a*) is sufficiently constant for a single v'' progression to justify the belief that the average of the two v''
sets, after (*b*) has been divided by the mean ratio (*b*)/(*a*), represents the intensities of the α bands of BO to about ± 5 per cent. This average is given in column (*c*). It would seem that no serious systematic errors due to absorption by the spectrograph, faulty calibration of the standard lamp or step slit, or properties of the photographic plate, are present. Evidently higher accuracy could be attained by multiplicity of measurements.

The fact that the mean ratio (*b*)/(*a*) is different for bands coming from the initial states 0, 1 and 2 must be taken to mean that the excitation conditions were not the same in both cases, so that a different distribution of the initial states occurred. This is perhaps due to the fact that the active nitrogen was produced by the discharge from an induction coil in (*a*) and from a 16,000-volt transformer in (*b*).

§ 4. COMPARISON WITH THEORY

Hutchisson (1) has evaluated the integral

$$I = \int_{-\infty}^{+\infty} \psi_{e'v'}(r)\,\psi_{e''v''}(r)\,dr$$ I, e, v

assuming the nuclei to perform simple harmonic oscillations, and in his second paper (2) has extended the results to the case where the potential energy of the nuclei is expressed as a power series in a factor depending on the displacement of the nuclei from their equilibrium positions. He also suggests the use of the wave function derived from Morse's potential-energy function⁽⁴⁾, and uses the method of graphical integration for determining I in this case for the molecule H_2*. Other wave functions in addition to these have been used by Price⁽³⁾, who has also used them to calculate the values of I for H_2.

I have calculated the values of the above integral for the BO α bands, using Hutchisson's formulae for harmonic oscillations, and have also determined them by graphical integration, using Morse's wave function; the molecular constants have been taken from Jevons' *Report on Band Spectra of Diatomic Molecules*⁽⁵⁾. As the calculations in the second method become rather laborious with increasing v, they have not been carried out for the 0–4 and 2–4 bands, which are of low intensity and hence are not so well determined experimentally as the others.

The intensity of an emission band is obtained by squaring I and multiplying by the fourth power of the frequency ν of the band and by the number of molecules in the upper state.

Table 1. α bands of BO

Band	λ	Intensity of band measured by method (*a*)	Intensity of band measured by method (*b*)	(*b*)/(*a*)	Average of (*a*) and of (*b*) divided by the mean value of (*b*)/(*a*)	Theoretical intensity $I^2\nu^4$	
						By harmonic wave function	By Morse's wave function
0–0	4248	64	94	1·47	64	67	57
0–1	4613	153	208	1·36	147	126	165
0–2	5040	135	193	1·43	133	134	139
0–3	5548	102	164	1·61	107	102	103
0–4	6160	54	84	1·51	56	63	—
				Mean = 1·48			
1–0	4036	141	186	1·32	142	184	136
1–1	4363	160	204	1·27	159	168	187
1–2	4744	79	100	1·27	79	71	72
				Mean = 1·29			
2–0	3847	†	323	—	115	254	153
2–1	4143	72	174	2·4	67	60	76
2–2	—	—	—	—	Absent	0·07	13
2–3	4883	42	115	2·7	42	20	31
2–4	5351	51	165	3·2	55	22	—
				Mean = 2·8			

This last quantity is quite unknown, and so theory and experiment can only be compared for bands with a common upper level. The values of $I^2\nu^4$ in table 1 have been multiplied by a factor which is constant for each v'' progression and is chosen so as to give the best fit between theory and experiment. It will be seen that the calculations based on harmonic oscillations and on Morse's wave function both agree well with experiment for bands for which $v' = 0$ and 1, but when $v' = 2$ Morse's function gives very much better results. Even with Morse's function, however, there is a systematic difference between calculated and experimental intensities when $v' = 2$.

---

* It should be pointed out that in Morse's paper, the denominator $\Gamma(s-1)$ in the normalizing factor should be $\Gamma(s+1)$.

† Absorbed strongly by the prism.

§ 5. ISOTOPE EFFECT IN α BANDS OF BO

It has been found possible to make a measurement of the intensity ratio of the bands of $B^{11}O$ and $B^{10}O$ for the 0–3 and 0–4 bands. As the isotopic bands are not completely separated the intensities of corresponding heads were measured, rather than the areas under the bands. The results for the intensity ratio of the isotopic bands are shown in table 2.

Table 2

	0–3 band	0–4 band	
Method (*a*)	3·8	3·5	Mean = 3·5
Method (*b*)	3·3	(Too faint)	

The correction (16, 17) to be made in the intensity ratio in order to obtain the relative abundance of the isotopes will be negligible here, as the bands both have v' equal to 0, and the energies of the $B^{11}O$ and $B^{10}O$ molecules differ very little for this level. The above result is in satisfactory agreement, for the relative abundance of the isotopes, with that for the β bands of BO, viz. 3·63.

§ 6. THE β BANDS OF BO

In a previous paper (9, 16) the writer has described the measurement of the intensities of the band heads in the β system of BO, and the determination (based on certain assumptions) of the probabilities of transition p between a number of vibrational states. This probability p is obtained by dividing the measured intensity of a band by ν^4 and by a factor proportional to the concentration of emitters in the particular v' state concerned. It should consequently be proportional to the square of the integral I given by Hutchisson, and the constant of proportionality should be the same for all bands in the system, irrespective of v'. Although no great precision was attempted in the measurement of the β bands* it seemed worth while to calculate I for a number of these bands, Hutchisson's calculations for harmonic oscillations being used. This was accordingly done; table 3 gives the value of I^2 below the corresponding value of p, and the values of I^2 have all been divided by a constant factor to make them comparable with p. Quite good agreement is to be found when $v' = 0$, and for the other progressions the agreement is fair. A notable discrepancy occurs for the 1–3 and 1–4 bands, and is too large to be accounted for by experimental error. It is very satisfactory to note that there is no systematic discrepancy between I^2 and p as v' alters. This may be taken to mean that the procedure ⁽¹⁶⁾ adopted for obtaining the number of emitters in the various v' states gives a substantially correct result. It may be mentioned that this point cannot readily be tested on the α bands, as it is necessary, in order to obtain the distribution of emitters in the initial state, that the intensities of all the bands in the system be measured. There is reason to believe that a considerable part of the α system lies in the infra-red beyond the range of the photographic plates used.

---

* The error is probably as high as ± 20 per cent in certain bands, though the error in the intensity ratios of neighbouring bands in a progression will be much smaller than this.

It would appear that in the β bands, as in the α bands of BO, the theory based on harmonic oscillations gives results which are in many cases in agreement with experiment, but that in certain bands the discrepancy between theory and experiment is greater than the experimental error. No doubt better agreement would be obtained if the theoretical intensities were calculated from Morse's energy function, but the accuracy of the measurements is hardly high enough to warrant the labour involved in these calculations.

Table 3. Transition probabilities in β bands of BO

v'' v'	0	1	2	3	4	5	6	7	8	
0	24 20	25 25	29 21	13 14	8 8					p I^2
1	25 37	6 10	— 0·6	21 7	22 56	15 12	11			p I^2
2	30 28	— 6·5	13 14	5 5	2 0·01	19 3	20	10		p I^2
3	17 10	16 29	— 0·6	4 6	20 9	— 0·9	8	21	14	p I^2

REFERENCES.

(1) E. Hutchisson. *Phys. Rev.* **36**, 410 (1930).
(2) E. Hutchisson. *Phys. Rev.* **37**, 45 (1931).
(3) W. C. Price. *Proc. R. S.* A, **136**, 264 (1932).
(4) P. M. Morse. *Phys. Rev.* **34**, 57 (1929).
(5) W. Jevons. *Report on Band Spectra of Diatomic Molecules*, 1932.
(6) L. S. Ornstein, W. J. H. Moll and H. C. Burger. *Objektive Spektralphotometrie*, Vieweg, Braunschweig, 1932.
(7) L. S. Ornstein. *Proc. Phys. Soc.* **37**, 334 (1925).
(8) N. Thompson. *Proc. Phys. Soc.* **45**, 381 (1933).
(9) A. Elliott. *The Optical Determination of the Relative Abundance of Isotopes*, Diss. Utrecht, 1930.
(10) C. W. W. Read and L. W. Johnson. *Phil. Mag.* **11**, 1152 (1931).
(11) H. A. Van Alphen. *Ann. d. Phys.* **85**, 1058 (1928).
(12) *Dictionary of Applied Physics*, vol. IV, p. 138.
(13) W. Jevons. *Proc. R. S.* A, **91**, 120 (1914).
(14) R. S. Mulliken. *Phys. Rev.* **25**, 259 (1925).
(15) W. E. Forsythe and A. G. Worthing. *Astrophys. Journ.* **61**, 146 (1925).
(16) A. Elliott. *Z. f. Phys.* **67**, 75 (1931).
(17) J. L. Dunham. *Phys. Rev.* **36**, 1553 (1930).

535·33·07:537·531

A HIGH-TEMPERATURE X-RAY CAMERA FOR PRECISION MEASUREMENTS

BY A. H. JAY, M.Sc., Beyer Fellow of the
University of Manchester

Communicated by Prof. W. L. Bragg, F.R.S., May 10, 1933.
Read July 7, 1933

ABSTRACT. A high-temperature X-ray camera has been designed for taking powder photographs which show well-resolved K_α doublets at high angles of reflection, enabling an accurate estimate of line position to be made. The temperature of the specimen was found in the following way. Photographs of silver, from which the lattice dimensions were calculated, were taken with varying heating currents. The coefficient of expansion of silver was used to convert lattice-spacing measurements to degrees centigrade. A curve relating the watts in the furnaces to the temperature of the specimens was thus obtained. A test of the reliability of the method was carried out by means of X-ray experiments on the expansion of quartz and the conclusion reached was that the assumption regarding the expansion of silver was valid. The temperature scale thus calculated was found to be correct to within 5° C.

§ 1. INTRODUCTION

CHANGES which may be found in the crystal structure of metals and alloys as the result of varying heat treatment do not always correspond to true equilibrium conditions. The time taken for an alloy structure to attain equilibrium varies enormously with the temperature. Equilibrium between neighbouring atoms may be established in a fraction of a second at temperatures just below the melting point, while in the case of high-melting alloys the attainment of equilibrium at room temperature is virtually impossible. Over a particular range of temperatures gradual changes take place during a finite period, and eventually equilibrium may be attained. Further transformation may be arrested if an alloy is suddenly cooled, and in some cases it may be possible to preserve the form characteristic of the temperature from which the alloy was quenched. At higher temperatures equilibrium is attained almost instantaneously, and here the structure cannot be retained by quenching. The use of a high-temperature X-ray camera is essential for temperatures above those at which quenching is applicable.

The pioneer X-ray investigations of alloy structures at high temperatures were those carried out by Westgren and Phragmen*. The camera was of the Debye-Scherrer type, the substance under examination being in the form of a wire which was heated to the required temperature by passing a current through the wire. Later workers† have used similar methods with cameras of slightly modified design. Becker has made measurements on the expansion of substances attached to a heated filament wire. In Cohn's experiments the substance was heated with a surrounding coil of wire.

---

* A. Westgren, *J. Iron and Steel Inst.* **103**, 303 (1921); A. Westgren, A. E. Lindh, G. Phragmen, *Z. f. Phys. Chem.* **98**, 181 (1921); **102**, 1 (1922).

† K. Becker, *Z. f. Phys.* **40**, 37 (1926); W. M. Cohn, *Z. f. Phys.* **50**, 123 (1928).

In designing the present high-temperature camera the aim was to preserve, as far as possible, the essentials of the powder-camera which the author has used and found highly satisfactory[*] and to introduce such heating and cooling elements as would not interfere with the photographing of the specimen.

§ 2. DESCRIPTION OF CAMERA

The camera is constructed in two main pieces, camera proper and detachable cover. The camera itself consists of two circular flanged discs held rigidly, in the form of a cylinder, by a block which contains the slit system for the entrance of the primary X-ray beam. The dimensions are: diameter of flanges, 9 cm.; total length of slit system, which is cylindrical, 2·5 cm.; entrance, diameter 3 mm.; exit, diameter 4 mm.; step with 2 mm. hole, 5 mm. from exit. The apex of the sides of the **V**-shaped block, figure 2 (*b*), is a vertical line 5 mm. in front of the axis of the camera. The knife edges, which give the sharp shadows on the X-ray film, are part of a plate which is permanently fixed on the central block, figure 2 (*b*), the knife edges being on the circumference of the camera flanges around which the X-ray film is wrapped. A cover plate is fixed over the knife edges, sufficient room being allowed for the film and paper covering to slide between it and them. An overlap of several mm. is essential for good contact of the film against the knife edges.

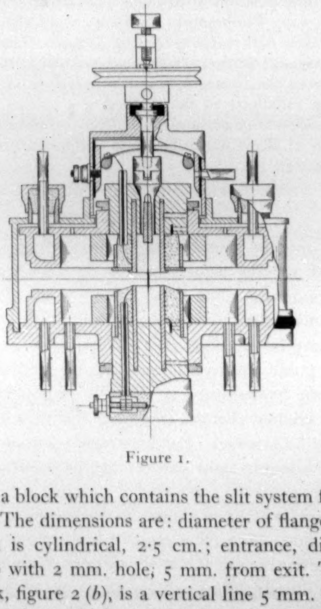


Figure 1.

---

[*] A. J. Bradley and A. H. Jay, *Proc. Phys. Soc.* **44**, 563 (1932). (Communicated to *Z. f. Krist.*)

The heating is provided by two small wire-wound furnaces, figures 3 (*a*), (*b*) whose position within the camera can be adjusted by the screw fitting and maintained by locking-nuts. The resistance wire* is wound around silica tubes which are held in steel blocks by small screws. In both furnaces one end of the wire is fixed to the block and this makes a common join with the rest of the camera when the furnaces are in position. Because the body of the camera forms part of the electrical circuit, the adjustable stand is insulated from the platform of the X-ray tube. The other end of the wire is in each case insulated by silica tubing and led to a terminal. For the lower furnace the terminal is fixed in a bakelite block on the exterior of the camera. In the upper furnace the wire is led to an insulated spring terminal of which details may be seen from figures 1, 3 (*b*). The shape of the block ends is such that only a small bend of the spring is needed for good contact with the insulated collar of the cover when the latter is in position. The necessary lagging for the furnaces is a mixture of equal parts of alumina powder and alundum cement. This has the advantage over alundum cement alone in that it avoids cracking due to excess shrinkage with repeated heating. An outer metal sheath provides the necessary strength.

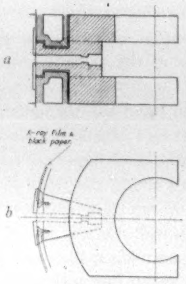


Figure 2*a*, *b*.

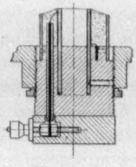


Figure 3*a*.

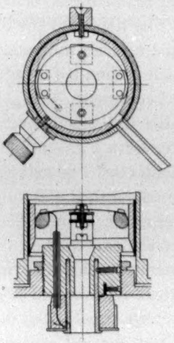


Figure 3*b*.

To maintain the X-ray film at room temperature, cooling is effected with two circular water-jackets round the inside of the camera flanges, each with its own inlet and outlet pipes, see figure 1. To ensure that the central strip of the X-ray film which is not in contact with the cold flanges shall not be heated by heat radiation, a screen is placed between the X-ray film and the specimen. This screen of light-proof black paper, strengthened by celluloid film, is wrapped round the small step as shown in figure 4 and held in position by rubber bands. The object of separating the inner black paper from the X-ray film is to allow the film to make contact with the knife edges, and thus enable a sharp shadow to be cast on the film by the general

* Resistance 4 ohms/yard, ¾ yard on each furnace.

X-ray scattering from the specimen. Experiments with furnace temperatures up to 1000° C. have shown that the arrangement works satisfactorily.

At the bottom of the camera are three tubes for gas inlet. Two are placed on the inner side of the water-jacket, 2 cm. on either side of the furnaces and opposite each other. The third tube allows the gas to enter the space between the film and the outside cover. Small holes in the top camera flange allow the gas to escape. When the camera is required for vacuum work these gas tubes may be used for evacuating it.

The steel specimen-holder rotates in the upper furnace block, figures 1, 5, in a ground cone joint which is made air-tight to prevent a disturbing stream of cold gas from flowing through the furnace. A silica rod, $\frac{3}{4}$ mm. in diameter, is held vertically in the holder, and on this the specimen is mounted and rotated in the path of the X-ray beam.

The details of the cover may be seen from figures 1 and 3 (*b*). The small upper dome encases the rotation gear and spring terminal, and serves to collect the gas which is then led away. Inside this dome is the insulated collar to which reference has been made. The collar is connected to an outside terminal. A pulley and shaft enable the specimen-holder to be rotated. The bearings of the pulley-shaft and cover form a ground joint which is effectively sealed with vacuum oil* contained in a small cup. The exit tube for the main X-ray beam is lead lined and the outer seal is made with a glass cover-slip. Glass is used in preference to metal foil since it gives no back-line reflection. To keep the cover light-tight a black paper cap is put over the end of the tube. A thick lead covering is placed round the front of the camera as a shield against penetrating radiation from the X-ray tube. The opening in the cover for the X-rays is sealed with thin aluminium foil. On the top of the cover are small tubes through which the water-pipes can pass. When the cover is in position the seal is made with rubber bungs held by screw caps. The cover makes a light-tight joint with the lower flange.

The two circular flanges are permanently united by the central block. The furnace blocks are screwed into a position where the X-ray beam from the slit system passes between the ends of the furnaces without striking them; with the given camera dimensions the separation of the two furnaces is about 4 or 5 mm. The furnace blocks are then clamped in position by locking-nuts. The protecting screen, consisting of the black paper and celluloid film, is wrapped round the camera on the steps as shown in figure 4 and is kept in position by rubber bands. Slots in the V-shaped central block allow an overlap which provides for the possibility of any small shrinkage of the paper and film due to heating.

When the specimen is being heated in a gas atmosphere the joint between the cover and the lower flange of the camera is sealed with plasticene. The flow of gas through the camera need not exceed 3 $cm.^3$/min. Where it is necessary to carry out the experiment *in vacuo*, the joint referred to above is made air-tight in the following way. A rubber ring is placed between the rim of the cover and the lower flange, and compressed by clamps. The camera is continuously evacuated with a rotary oil pump.

---

* Apiezon J, made by Shell-Mex Ltd. under Metro-Vickers patents.

§ 3. METHOD OF HEATING THE SPECIMEN

One of the advantages possessed by a high-temperature camera in which the specimen is heated with a surrounding furnace instead of a filament wire through its centre is that a much more uniform temperature can be obtained throughout the scattering mass. With central-wire heating the specimen acts as a lagging for the hot wire and there is an appreciable temperature-gradient from the centre outwards. With different specimens this will be an unknown and variable factor. In the case of materials such as refractories, where the absorption is comparatively low, the scattering takes place throughout the whole mass. A photograph of a specimen heated in this way would show a lack of definiteness in the lines, due to the superposition of slightly varying patterns. Moreover the temperature of the outer layers, which effect most of the scattering, is not that of the filament, the lattice spacing of which cannot be taken as a sure guide to the temperature of the specimen.

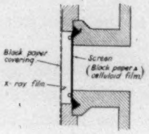


Figure 4.

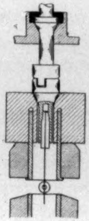


Figure 5.

§ 4. EXPERIMENTAL

The choice of a substance for mounting the powder grains as a cylindrical specimen presents some difficulty. Among the substances suggested by previous workers are water-glass, gypsum, zirconia and porcelain products. The list is somewhat limited and the final choice depends largely on the material to be investigated. This binding substance must not add unnecessary X-ray spectra or cause contamination of the specimen by chemical reaction. Water-glass as an adhesive appears to have been favoured, but the possibility of reaction with the powdered specimen must not be overlooked.

The following method of mounting the powder has proved very satisfactory. The thin silica rod, $\frac{3}{4}$ mm. in diameter, which is used in supporting the specimen is ground to $\frac{1}{3}$ mm. near its lower end. At the other end the rod is fused to make a bead by which it is supported in the holder. The silica rod is thus held in a vertical position and along the axis of rotation of the holder. Good centering, giving a minimum of lateral movement during rotation, is essential and is obtained by a good fit of the rod in the holder chuck. The powder is fine enough to pass through a 250-mesh sieve, which gives particles less than 0·05 mm.; it is mixed to a paste with a very dilute solution of gum arabic and is applied as a coating around the narrow part of the rod. The gum acts as an adhesive until it chars, at a temperature which may be of the order of 200° C. For higher temperatures the gum acts as a temporary binding, and subsequently the grains hold together by sintering. The amount of carbon formed is exceedingly small, and in our experiments it was burnt away in an atmosphere of hydrogen. Photographs of specimens at temperatures of 800° C. have been taken and it has been found that the powder has adhered.

Procedure. The specimen powder is mixed to a paste with a dilute solution of gum, is applied as a coating over the narrow part of the silica rod as described above, and is afterwards placed in position in the camera. The specimen-holder makes a gas-tight joint with the steel block.

The camera is loaded in a photographic dark room, where the cover is put in position and the seal between the water-pipes and cover is made by means of rubber bungs held by screw caps. Finally the seal between the cover and the lower flange is made.

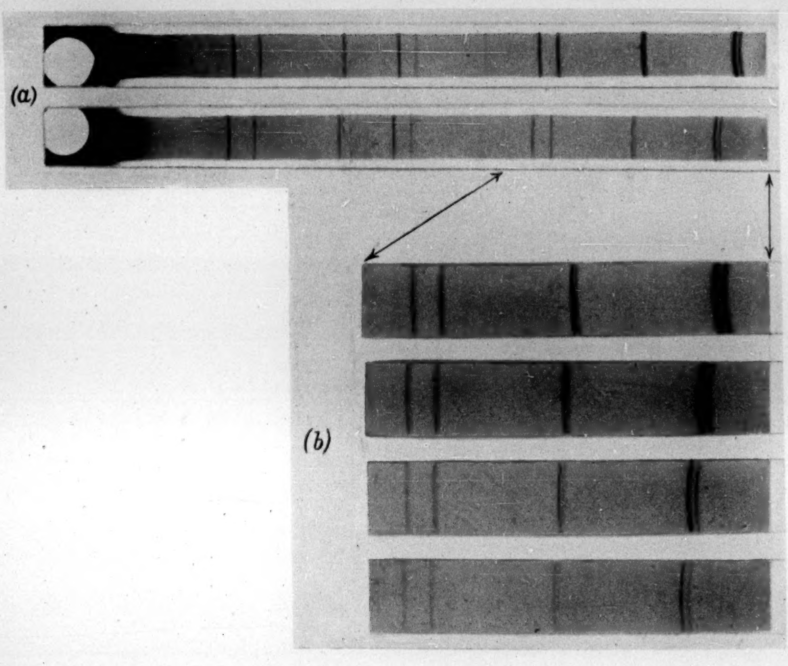
The procedure for adjusting the camera in front of the X-ray tube is similar to that of our standard powder-camera. One preliminary adjustment of the camera and stand is sufficient for a series of experiments as the stand is provided with pivot points.

When the camera has been placed in position the water and gas supplies and electrical leads are connected. The water is supplied from a constant head, the flow being 350 cm^3/min. through each flange. The heating current through the furnaces is raised to the required value and maintained there for a definite time. The specimen is rotated by the pulley drive during the whole of the exposure, a complete rotation being made every few seconds. The exposure-time depends on the substance under investigation and on the radiation employed. With a tube current of 30 mA. at 52 kV. the times range from 5 minutes, for Al, Ni, Cu, Fe and Ag, to $\frac{3}{4}$ of an hour for rock salt and silicates, for characteristic K_α radiation, β radiation being eliminated with a screen.

§ 5. RESULTS. THE RELATION OF ENERGY INPUT INTO THE FURNACES AND THE TEMPERATURE OF THE SPECIMEN

One of the aims of the camera design was to make it possible to reproduce temperature conditions by using a known heating current. For this purpose the furnaces are strongly made, and throughout the whole series of experiments the flow of water through each water-jacket is maintained constant. The small gas stream through the camera is not sufficient to disturb the temperature conditions, being away from the furnaces. The outside of the camera is quite cold, so that radiation losses from the camera are negligible.

To find a relation between energy-input and the temperature of the specimen the following method is employed. An X-ray photograph of a standard material, pure silver, is taken for a given heating current in the furnaces. This procedure is repeated under varying heating conditions. From measurement of the position of the K_α doublets at high angles of reflection an accurate value of the lattice spacing



Powder photographs of pure silver.

corresponding to a measured heating current is obtained by means of the $\cos^2 \theta$ method* of extrapolation.

From the results a graphical relation between energy input and lattice spacing is obtained, figure 6. We now make the assumption that the coefficient of thermal expansion of silver as obtained by direct measurement is the same as that for the expansion of the atomic lattice†. In a later paper‡ we shall show from measurements on the expansion of quartz that this assumption is valid. It might be possible that both silver and quartz have the same difference between X-ray and optical dimensions, but it is unlikely that they would vary with temperature in exactly the same way along both the axes of quartz. Such a supposition is certainly not supported by the results for quartz, where the α-β change point is found at 579° C., for this agrees, within the limits of experimental error, with the acknowledged temperature, 575° C. The coefficient of expansion of silver as found by Scheel§ was used to convert lattice spacing to degrees centigrade. A temperature scale is included in the figure.

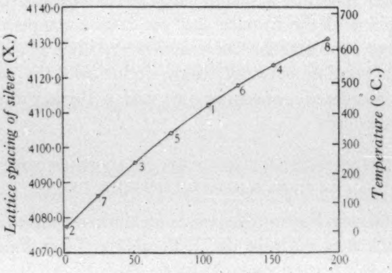


Figure 6.

To test the consistency of the observations the conditions were chosen at random, the order in which the photographs were taken not being the order of increasing temperature. This gives an opportunity of detecting any systematic change in the furnaces after heating. The same specimen was used throughout the experiments and no indication is given by the graph, figure 6, of any departure from a smooth curve, such as might be expected if a factor depending on time was present. The numbers opposite the points on the graph denote the order of the experiment, the order with increasing temperature being 2, 7, 3, 5, 1, 6, 4 and 8. Thus the method appears to be reliable, definite temperature conditions being obtained from definite heating currents. Granted that temperature can be calculated from spacing measurements, the temperatures are probably accurate to 3° C.

---

* A. J. Bradley and A. H. Jay, *Proc. Phys. Soc.* **44**, 563 (1932).

† Compare F. Zwicky, *Proc. Nat. Acad.* **15**, 253; 816 (1929), *Hel. Phys. Acta*, **3**, 269 (1930), and A. Goetz and R. C. Hergenrother, *Phys. Rev.* **40**, 137, 643 (1932).

‡ A. H. Jay, Communicated to the Royal Society, May 6, 1933.

§ K. Scheel, *Z. f. Phys.* **5**, 167 (1921).

Below the complete photographs of silver at (*a*) in the plate is shown at (*b*) a series of enlargements of that part of the film which is measured for the determination of the lattice spacing. The photographs show the inward displacement of the lines for rise of temperature. In addition, the effect of temperature in reducing the intensity of the high-order reflections can be seen from a comparison of the end lines in succeeding photographs.

It might be thought surprising that a thermocouple has not been used to measure the temperature. There are several reasons for the omission of a thermocouple in the present case. One is the difficulty of placing the couple at the exact position occupied by the specimen. Another is that since the couple is heated by radiation, the conductivity of the leads would result in its having a lower temperature than the specimen. The difference would be a doubtful quantity and variable with the temperature. It might be possible to place the thermocouple at some convenient point of the furnace and use it as a temperature-pointer when once the camera had been standardized. However, since it was found that there was such a simple relation between energy-input and the temperature of the specimen it was considered unnecessary to add a further complication by the addition of a thermocouple.

§ 6. ACKNOWLEDGMENTS

I wish to thank Messrs Kay and Reynolds for their assistance in the construction of the camera which was made in the Laboratory. I am indebted to Dr A. J. Bradley for his helpful discussions and also to Prof. W. L. Bragg, F.R.S., for his encouraging interest in the work, which was carried out in the Physical Laboratory of the University of Manchester. I also thank Mr A. P. M. Fleming, C.B.E., Director-Manager, Research and Education Department of the Metropolitan-Vickers Electrical Co. Ltd., for his interest and for permission to publish the work.

535·243·07

CONDITIONS FOR SECURING ACCURACY IN SPECTROPHOTOMETRY

By F. TWYMAN, F.Inst.P., F.R.S.
AND
G. F. LOTHIAN, B.A. (Oxon.)

Received April 25, 1933 *and in revised form May* 31, 1933. *Read July* 7, 1933

ABSTRACT. The paper sets forth basic principles in the design and use of spectrophotometers. §§ 1–4 deal with absorption spectrophotometry in its application to chemistry and includes consideration of the various methods in use, viz. photographic, visual, and photoelectric. The optimum conditions for each method are stated and the three types of method are compared. § 5 is concerned with spectrophotometry as a means of describing a radiation, as for instance in connexion with colorimetry, the comparison of light sources and quantitative spectrum analysis.

---

§ 1. THE PURPOSES OF SPECTROPHOTOMETRY

The radiations which enable one to discriminate between substances (as in most of the applications in chemistry, such as the estimation of dyes and other absorbing substances) are those which are most absorbed. The radiations which chiefly determine a colour are, on the contrary, those which are most copiously present.

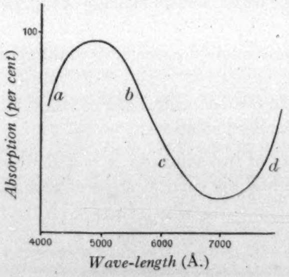


Figure 1.

For example, if a substance has the absorption curve shown in figure 1, the portion of the curve of outstanding importance as distinguishing the absorbing substance is that marked from *a* to *b*: yet in producing colour, that portion marked *c* to *d* is of paramount importance. In this paper we consider separately these two purposes to which spectrophotometry may be applied.

The measurement of absorption. The function of absorption that is appropriate

ϵ

for this purpose is the Roscoe-Bunsen extinction coefficient ϵ, which for any substance and wave-length is, according to Beer's law, proportional to the concentration of the absorbing material. Thus the proportional accuracy with which a substance can be characterized by its absorption follows that with which ϵ can be determined, and is represented by $\Delta\epsilon/\epsilon$ where $\Delta\epsilon$ is the smallest measurable increment of ϵ.

$\Delta\epsilon$

The measurement of a radiation. A radiation, on the other hand, is best characterized by its intensity, and the proportional error of its measurement is represented by $\Delta I/I$, where ΔI is the smallest measurable increment of I, the intensity of the radiation.

We shall examine separately these two classes of measurement, which require differing modes of attack if the highest accuracy is to be attained.

§ 2. THE CHARACTERIZATION OF A SUBSTANCE BY ITS ABSORPTION

The type of problem we have in mind here is well illustrated by the application of absorption spectrophotometry to chemical analysis. It will be useful to give examples of this, and then to continue with a few considerations which are common to all methods of spectrophotometry.

The algebraical expression of Beer's law, and its use in the analysis of absorbing solutions. It has long been known how, if one has a mixture of two absorbing substances whose absorptions are known for two wave-lengths, to obtain by the application of Beer's law the proportions in which the two substances are present in the mixture*. What follows is the procedure described in the reference, with a very simple corollary thereto.

The following nomenclature will be used:

$\alpha_0, \alpha_1, \beta_0, \beta_1$
λ_0, λ_1

Let $\alpha_0, \alpha_1, \beta_0, \beta_1$ be the extinction coefficients of mixtures α, β, for wave-lengths λ_0, λ_1.

a_0, a_1, b_0, b_1

Let a_0, a_1, b_0, b_1 be the extinction coefficients of the component solutions A, B... for wave-lengths λ_0, λ_1.

$_\alpha, m_\beta, n_\alpha, n_\beta$

Let $m_\alpha, m_\beta, n_\alpha, n_\beta$, be the concentrations of solutions A, B, in mixtures α, β, in terms of that of the standard solutions.

Example 1. A mixture of two solutions A and B whose absorption curves are known. It is required to find the concentration of each solution in the mixture.

By Beer's law:

$$\alpha_0 = m_\alpha a_0 + n_\alpha b_0,$$

$$\alpha_1 = m_\alpha a_1 + n_\alpha b_1,$$

from which

$$m_\alpha = \frac{\alpha_0 b_1 - \alpha_1 b_0}{a_0 b_1 - a_1 b_0},$$

and

$$n_\alpha = \frac{\alpha_0 a_1 - \alpha_1 a_0}{b_0 a_1 - b_1 a_0}.$$

---

* See K. Vierordt, *Die Anwendung des Spektralapparates zur Photometrie der Absorptionsspectren und zur quantitativen chemischen Analyse* (Tübingen, 1873); on p. 51 Vierordt describes how he checked the method on a mixture of potassium permanganate and potassium dichromate.

See also K. Vierordt, *Die quantitative Spektralanalyse in ihrer Anwendung auf Physiologie, Physik, Chemie, und Technologie* (Tübingen, 1876), for an account of work on absorption spectrophotometry.

It will be observed that to find m_α and n_α we only need to know the extinction coefficients of solutions A and B and of the mixture for two wave-lengths. The wave-lengths need to be selected with consideration in each specific problem, in order that high accuracy may be attained in the determination of m_α and n_α.

Example 2. Mixtures of two substances A and B, the absorption curve of only one of these being known.

If one makes observations on a number of such mixtures (α, β, γ, etc.) in which the concentrations of the substances A and B are different, then one is able to determine the ratio of the concentrations of the unknown substance B in any two of these mixtures.

As in example 1, we can write down two equations for a mixture:

$$\alpha_0 = m_\alpha a_0 + n_\alpha b_0,$$
$$\alpha_1 = m_\alpha a_1 + n_\alpha b_1.$$

Similarly we have two equations for another mixture:

$$\beta_0 = m_\beta a_0 + n_\beta b_0,$$
$$\beta_1 = m_\beta a_1 + n_\beta b_1.$$

In these four equations, there are six unknowns, m_α, n_α, m_β, n_β, b_0, b_1, so that a complete solution is impossible.

Nevertheless, the form of the equations enables one to obtain one piece of useful information, namely, the ratio

$$\frac{n_\alpha}{n_\beta} = \frac{\alpha_0 - (a_0/a_1).\alpha_1}{\beta_0 - (a_0/a_1).\beta_1}.$$

As an example of a problem to which this would be applicable, we may mention ethocaine. This substance is stated to hydrolyse slowly in aqueous solution. A direct application of the above test would therefore allow one to investigate the progress of the decomposition.

As a concrete case, we may consider the curves of figure 2. Curves 1, 2 represent the absorption of two mixtures of an unknown substance, in different proportions, with benzoic acid. Curve 3 represents the absorption of a solution containing benzoic acid only.

In the case in which $\lambda_0 = 2500$, $\lambda_1 = 2800$, we can obtain from the curves:

$$\alpha_0 = 0{\cdot}525, \quad \alpha_1 = 1{\cdot}14.$$
$$\beta_0 = 0{\cdot}395, \quad \beta_1 = 1{\cdot}62.$$
$$a_0 = 0{\cdot}565, \quad a_1 = 0{\cdot}59.$$

Substituting in the expression obtained we find that

$$\frac{n_\alpha}{n_\beta} = \frac{0{\cdot}525 - 1{\cdot}09}{0{\cdot}395 - 1{\cdot}55} = \frac{0{\cdot}565}{1{\cdot}155} = 0{\cdot}489.$$

The choice of the most suitable pair of wave-lengths for analysis. The accuracy attained in a method of analysis such as the above will also depend considerably on the choice of the wave-lengths. The question is not susceptible of a finite method of analysis, because one does not know the equations to the curves obtained. The best way is to use the method of trial and error, in conjunction with careful inspection of the curves and of the form of the equation giving the required solution.

As an example, one can consider the calculation above based on the formula

$$\frac{n_\alpha}{n_\beta}=\frac{\alpha_0-(a_0/a_1).\alpha_1}{\beta_0-(a_0/a_1).\beta_1}.$$

Suppose that the "probable numerical error" in each of the above quantities on the right-hand side has the same constant value irrespective of the magnitude of the quantities themselves. Then the probable numerical error in the value of the numerator is constant, so that to make the fractional error small the numerator should have as large a value as possible. Thus we should endeavour to choose values so that *the difference between the two numerator terms is as large as possible*, and also that between the two denominator terms.

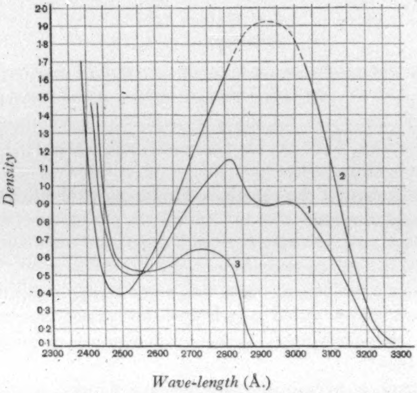


Figure 2.

Supposing we have $\alpha_0 > \alpha_1$, then a_0/a_1 should be small; similarly, one requires that β_0/β_1 should also be as great as possible. Thus in a general way the suitable conditions are that α_0/α_1, β_0/β_1 must be as large as possible, with a_0/a_1 as small as possible, or alternatively α_0/α_1, β_0/β_1 must be as small as possible with a_0/a_1 as large as possible. From figure 2 these conditions are apparently best attained at $\lambda_0 = 2500$, $\lambda_1 = 2800$.

Alternatively the wave-lengths might be chosen by direct consideration of the condition set out above in italics. Thus, in the numerator of the calculation given as an example in example 2 above, the difference 0·565 is comparable with both 0·525 and 1·09. If, instead, wave-lengths 2500 and 2600 had been chosen, the corresponding figures would have been 0·525 − 0·64, or − 0·115, from curves of figure 2.

In the case actually calculated an error of 0·01 (see p. 650) in density would cause an error of about 2 per cent in the final answer, but with the second pair of wave-lengths an error of 0·01 in density would involve an error of as much as 10 per cent in the final answer.

The dispersion system. The points of an absorption curve where great accuracy is required (such as those chosen above) will often be on the slope of the curve, so that if the measurements made on different occasions are to correspond we must ensure that the wave-lengths used are always the same, within the limit of the following condition: *The error of density due to error in wave-length setting should be less than the error in the density as measured.* Thus, in making use of a continuous spectrum, an instrument of sufficiently high dispersion is needed; and the steeper the curve at the point under consideration, the greater the dispersion desirable.

To take an illustration: in the use of a visual spectrophotometer for determining small percentages of carboxyhaemoglobin in blood, useful accuracy can only be attained by making measurements near the two wave-lengths 5600 and 5770 Å. At the latter wave-length the spectrophotometric curve of carboxyhaemoglobin is so steep that very narrow slits must be used in order to get a spectrophotometric measurement which has useful meaning.

In consequence of small brightness at large densities, it may sometimes be desirable to increase the width of the collimator slit. Where the source has a line spectrum this slit can be opened considerably without sacrifice of purity of spectrum, for one can then use the same lines on each occasion so that the above condition as to wave-length setting is automatically fulfilled. With a continuous-spectrum source, however, one must effect a compromise between the best light-intensity and the desired purity of spectrum.

Light-source. In all methods of visual or photographic spectrophotometry in which the intensities of two closely adjacent spectra are compared, it is essential that the relative intensities of such spectra should depend only on the absorption of the absorbing substance which is placed in one beam, and the deliberate variation of intensity which is imposed on the other beam.

An essential condition for accurate spectrophotometry with the types of instrument which the present authors consider best for this work is that the rays which have passed through the middle of the slit (which corresponds with the point of the spectrum where comparisons of intensity are made) should pass through the spectrograph *without any vignetting*. That this condition is fulfilled can be tested by looking through the spectroscope after removal of the eyepiece at an image of the light-source, the whole of which should be seen within the aperture of the apparatus. A corresponding test can be made with a spectrograph.

The light reaches the spectroscopic apparatus through two separate optical paths, so that if the photometric part of the apparatus is out of adjustment two such images of the light-source, not quite coincident, may be seen. If, then, the light-source is out of centre one of the images may be vignetted even if the other is not, or one may be vignetted to a greater extent than the other. In this way, a difference may be introduced between the effective relative intensities of the two beams.

It is thus necessary to have the light-source *small enough to be included within the aperture of the spectroscope or spectrograph.* This is even more necessary when, as usually occurs in ultra-violet spectrophotometry, there is very considerable chromatic aberration in the lens systems of photometer and spectrograph. But in order to obtain high accuracy large densities must be used, for these are needed for high accuracy in the characterization of substances by means of their absorption; and consequently as strong an intensity of illumination as possible must be obtained. But only by filling the aperture with light can the intrinsic brightness of the light-source be fully utilized. Thus the condition stated above in italics is antagonistic to the condition for high accuracy in the measurement of extinction coefficients.

Were it possible to obtain a light-source of great intrinsic brightness which at the same time was entirely uniform in radiation per element of its radiating area, the best course to adopt would be to produce an image which would entirely fill the aperture at all wave-lengths. Such a light-source, however, only exists in the form of an enclosed chamber within which the light-source is situated, and with such a means of illumination the intrinsic brightness is insufficient to give accuracy in those measurements of absorption with which we are now concerned. Thus the condition to be aimed at is that the trace of the light-source should pass through the spectroscope without being vignetted, but with no more margin than is needed to provide for any excentricity that may be accidentally present.

Similar considerations are applicable in the objective methods of spectrophotometry using photo-electric cells and the like.

The accuracy with which cells for spectrophotometry should be made

Visual and photographic measurements. The accuracy of the cells should be such that the departure from the nominal length of liquid should cause no measurable error. The least error in a density-measurement likely to be achieved in practice is probably equal to ± 0·005 in the density-reading. At a density of, say, 1·5, this is equal to 0·3 per cent. Thus the error should not be greater, for the best work than, say, one-half of this, i.e. 0·15 per cent.

Photo-electric measurements. As will be shown on p. 653, the best density to measure with a photo-electric null method is 0·4343. In measuring such a density a very much greater *sensitiveness* of measurement can be attained than with either visual or photographic methods. Those who have made careful comparisons of such measurements with those attained by the most careful visual spectrophotometry are agreed that absolute measurements of density made by photo-electric null methods do not yet yield an accuracy in accordance with this degree of sensitiveness*; but however this may be it will be seen that, in measuring a density of 0·4343, cells with an accuracy of ± 0·15 per cent will not be responsible for an error of extinction coefficient greater than that which corresponds with an error of ± 0·00055 in the density-measurement. Not till an accuracy of density-measurement approaching this is expected will any higher accuracy of cell become necessary.

The accuracy required in setting up the cell. Unless the cell is set every time perpendicular to the light beam, the length of light-path through the absorbing
i medium will vary. Suppose that the normal to the cell makes a small angle *i* with

---

* See p. 653.

the incident light beam. If μ is the refractive index of the absorbing medium, it is easily seen that the fractional error δ in the path is given by

$$i = \mu\sqrt{(2\delta)}.$$

For instance, if $\mu = 1{\cdot}3$ and $\delta = 0{\cdot}0015$ then $i = 4^\circ\,6'$. Thus the cell should be set with its plane perpendicular to the light ray to within 4°.

With very little trouble, the cell can be set to 1°, so that the error due to this setting should always be negligible although special attention to this point is required with short cells. The length of cell used should be chosen to obtain a density approximately to the optimum value for the method used; and different cells may often be used with advantage for different portions of the same absorption band.

Effect of temperature. In some cases, absorption varies very considerably with temperature*. It is thus important in any particular case to ascertain by trial if such an effect is present, in which case steps should be taken to ensure that measurements are taken at a temperature sufficiently constant for any error introduced in this way to be negligible compared with other sources of error.

§ 3. THE VARIOUS MEANS OF PHOTOMETRY

We must now consider broadly the means of photometry which are available, and what is the best way to employ each in order to determine extinction coefficients. The means we shall consider are the following: (*a*) Photographed pairs of spectra examined visually; (*b*) photographed pairs of spectra examined by microphotometer; (*c*) visual photometry; (*d*) direct measurement by objective photometer employing photo-electric, selenium or photronic cells, thermopiles or bolometers.

Photographic means of photometry, (*a*) *and* (*b*) *in the above classification.* In photographic methods of spectrophotometry, in which two juxtaposed photographs of spectra are compared visually, the differences in density of blackening which it is possible to detect are of the order of, say, 0·06.

It has long been known that for neighbouring areas of a photographic plate and for a constant time of exposure, the density of blackening of the plate is related to the log of the intensity, I, of the incident light in the way shown by the curves of figure 3.

The ratio of the increase of the density of blackening to the increase of light intensity (i.e. the slope of the curve) is greatest on the straight portion of the curve, where it is given a special name, γ. Thus, in making photometric measurements, a plate and method of development (which latter is also very important) giving a large γ is desirable†, as at *a*, figure 3. On the straight portion of the curve the smallest detectable change in $\log_{10} I$ is obviously given by the smallest detectable difference in density of blackening divided by γ. If a plate having a value of γ equal to 6 be used, then it should be possible to detect a difference in the density of the absorbing substance equal to 0·06 ÷ 6, or 0·01, *and we find that this is confirmed by experiment.*

---

* Mukerji, Bhattacharji and Dahr (*J. Phys. Chem.* **32**, 1834 (1928); *J. Phys. Chem.* **35**, 653 (1931)). In the former paper is recorded a case where a 30° rise of temperature caused an increase of density of about two and a half times.

† The table in the Appendix shows that the most suitable Ilford plate would be the panchromatic half-tone. The Eastman plates recommended are (*a*) Panchromatic-Wratten M (III-B), or alternatively III-F. (*b*) Where panchromatism is not desired, Wratten Metallographic or III-H. (*c*) For the ultra-violet region, III-F, III-H, or III-O, treated by the ultra-violet-sensitizing method. The most suitable developer for all the above plates is that listed by Eastman as D. 19. For brevity we shall subsequently refer to the combination of plate and development simply as "plate."

With a large γ the range of correct exposure (given by the straight portion *cd*, figure 3) is smaller, so that if a plate of large γ be used one must adjust the exposure of the part of the spectrum where a match is being made in accordance with the spectral distribution of the light-source and the sensitivity of the emulsion to different wave-lengths, in such a way that one is working on the portion *cd*, figure 3.

For preliminary surveys one will require a plate with a large latitude *c′d′*, figure 3; that is, a plate with small γ*. In this case, however, the measurement of densities will be much less accurate. A list of γ values for various plates and developers is given in the Appendix.

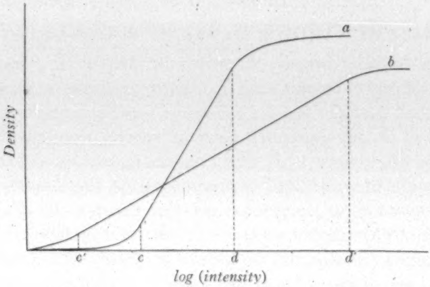


Figure 3.

It has been held that by visual examination of such photographs as those in question, densities can be measured to within 0·02 to 0·04, *independently of the absolute value of density*†. As we have seen, this considerably underestimates the accuracy that can be attained, but in any case it remains true that in order that the percentage error in the measurement of the density should be small in photographic spectrophotometry, *the density itself should be large.* It has in the past been very usual to work with densities not exceeding 1·5, but this seems frequently to have been due to the instruments available rather than to any more fundamental reason.

In the use of large densities with a rotating-sector photometer the large number of long exposures required will cause a serious increase in the time required to obtain an absorption curve. Further, the accuracy in making such sectors does not usually justify the measurement therewith of densities greater than 1·5. In using the notched échelon cell*, however, only one exposure is required to obtain a number of readings so that the measurement of relatively large densities does not take unduly long. Further, any error in the rotating sector does not alter the shape for the resulting curve of extinction coefficients, all the ordinates being in error in the same proportion.

---

* The most suitable Ilford plate here is the Hypersensitive Panchromatic. Eastman Kodak recommend (*a*) Panchromatic—I-F. (*b*) Non-panchromatic—Eastman D.C. Ortho (I-H) or Wratten Hypersensitive. (*c*) Ultra-violet—I-F. A suitable developer in this case is D-76-C.

† See H. von Halban and J. Eisenbrand, *Proc. R. S.* A, **116**, 154 (1927).

To take an example, if in the use of an échelon cell of greatest length 1 cm. the density of liquid measured is 0·3, giving us extinction coefficients from 0·3 to 3 and requiring an exposure of about 5 seconds, we may get an error of from 7 to 13 per cent in the measurement of the density, and a like error in the values of the extinction coefficients†. If, however, the density of liquid measured is 1·5, giving extinction coefficients from 1·5 to 15 and requiring an exposure of about 1¼ minutes, the error will not be more than from 1½ to 3 per cent. Thus the échelon cell is at its best in conjunction with high extinction coefficients. Where a low extinction coefficient must be measured a photometer which permits the use of a cell of greater length should be used. The employment of photo-electric instead of visual means of comparing the pairs of spectra does not alter the above conclusions.

Dobson‡ describes a method of photometry to which the same fundamental principles apply. In this a neutral-tint wedge is placed in front of the plate or the slit of the spectrograph, the gradient of the wedge being parallel to the length of the slit. A standard source is exposed on each plate as well as the spectra under investigation, and the points at which the density of blackening of the spectrum is equal to that of the standard are determined by means of a photometer. An objection to this method is that points to be compared are not closely adjacent on a plate, so that possible irregularities of development and plate are in this method a source of error.

Visual means of photometry, (c) in the classification on p. 649. The percentage error in a density-measurement made by a match with the eye is smaller the higher the density§, as in the photographic method, with the following limitations:

(1) The sensitivity of the eye to a given small percentage difference in brightness falls off at low brightnesses. This is specially noticeable at the violet end of the spectrum where the eye, the light-source, and the increased dispersion of the spectrometer act together in producing a small brightness. This last can be overcome without unduly sacrificing the purity of the spectrum, by using for the violet a wider front slit than in other parts of the spectrum. Very great advantage is derived from placing an appropriate filter immediately in front of the slit, or outside the

---

[*] For account of the cell see F. Twyman, L. J. Spencer, A. Harvey, *Trans. Opt. Soc.* **33**, 37 (1931–32); and F. Twyman, *Proc. Phys. Soc.* **45**, 1 (1933).

[†] Dobson, Griffiths and Harrison, *Photographic Photometry* (1926).

[‡] It is assumed that the cell is made or measured with sufficient accuracy for the errors in thickness to be negligible. See p. 648.

[§] It easily follows from the Weber-Fechner law that the smallest detectable change of density (ΔD) has a constant value independent of the absolute value of density.

eyepiece in order to absorb the scattered light of wave-lengths which are transmitted freely by the substance under test.

(2) In the case of some visual spectrophotometers it is found possible to obtain an accuracy of about 0·005 in density-measurements by taking a number of observations, this residual error being due to the limit of sensitivity of the eye. Under these conditions, for densities of about 2·0 the scale usually becomes so cramped with forms employing Nicol prisms that there is in addition an error in reading the scale of about the same magnitude (0·005). For this reason densities of between about 1·5 and 2·0 give the best accuracy*.

For the most accurate work a density-reading is accompanied by a reading of the zero for the particular wave-length in question. The accuracy of density-measurement can then be increased by taking readings with the absorbing medium first in one beam and then in the other; the density is half the difference between the two readings. By reading on the opposite side of the zero instead of on the zero itself one obtains twice the accuracy with the same number of readings, i.e. with the same expenditure of time.

Objective means of photometry, (*d*) *in the classification on p.* 649. One can use a
photo-electric method† to measure the absorption of a medium. The sensitivity of
such an arrangement is defined by the smallest change in light-intensity which can
$\Delta\theta$ be measured. In a given arrangement suppose $\Delta\theta$ to be the smallest detectable
θ change in the value of the deflection θ of the galvanometer or other indicating instru-
ΔI ment. Then ΔI, the smallest detectable change in light-intensity, is given by
k $\Delta I = k\Delta\theta$, k being a constant for the particular arrangement. Thus, in photo-electric
measurements with a given apparatus ΔI has a constant value independent of the
I intensity I of the transmitted light, in contrast to the eye and photographic plate, for
which, within limits, $\Delta I/I$ has a constant value.

The condition for greatest accuracy in absorption-measurements is that the per-
centage accuracy in the measurement of an extinction coefficient shall be a maximum.
D, ΔD This implies a minimum value for $\Delta D/D$, where D and ΔD are, respectively, density
and the smallest detectable change in density.

I_0, I If I_0 is the intensity of light incident on the absorbing medium and I the amount
transmitted into the measuring apparatus, then the density is given by

$$D = \log_{10} I_0/I \qquad \ldots\ldots(1).$$

On differentiation this becomes

$$\Delta D = -\log_{10} e \,.\, \Delta I/I \qquad \ldots\ldots(2).$$

$$\therefore \quad \frac{\Delta D}{D} = -\frac{\log_{10} e}{ID} \,.\, \Delta I$$

$$= -\frac{\log_{10} e}{I_0 D \,.\, 10^{-D}} \,.\, \Delta I \qquad \ldots\ldots(3).$$

---

* The scale of the spectrophotometer described by Dowell in *J. Sci. Instr.* **8**, 382 (1931) and *J. Sci. Instr.* **10**, 153 (1933), which follows a $\tan^4$ law, enables densities above 2 to be used with advantage.

† In which we must be understood also to include the other objective methods mentioned.

To find the optimum value of D we must find when expression (3) has a minimum value, i.e. when $D.10^{-D}$ from (3) has a maximum value.

Thus, differentiating and equating to zero we get $D = 1/\log_e 10 = 0{\cdot}4343$, so that the best density to use is 0·4343. We can see how critical this value is by examining the following values of the expression $D.10^{-D}$ from equation (3).

$D.$	1	0·8	0·43	0·2	0·1
$D.10^{-D}$	0·100	0·127	0·159	0·126	0·079

Thus we may use densities between 0·2 and 0·8 without any considerable loss of accuracy. The above remarks apply in general to photo-electric methods, whether null or deflection methods. But in any particular instrument other features of design might cause one to depart from this condition.

There is no doubt that photo-electric methods give much greater sensitivity of discriminating between two radiations than the eye. The balance of evidence published by those competent to judge seems still on the whole to indicate that as far as absolute measurements are concerned, visual methods are more to be relied upon than photo-electric ones. It should be mentioned too, that besides the electrical circuit, the photometric devices (wedges, sectors, etc.) may also impose limits on both accuracy and sensitivity. The present writers consider, however, that in due course the systematic errors in photo-electric instruments that lead to such a state of affairs will be eliminated.

§4. APPLICATION OF THE ABOVE PRINCIPLES, AND COMPARISON OF THE VARIOUS INSTRUMENTAL METHODS TO SPECIFIC EXAMPLES

The measurement of extinction coefficients in the ultra-violet. We shall assume throughout that we can increase the density of the substance under test to any degree that may be desirable, which can usually be done without difficulty by taking a more concentrated solution or a greater thickness of the absorbing substance.

(*a*) Photographed spectra examined visually. With a quartz spectrograph of the Hilger E. 3 type and the usual sparking set* and photographic plate and development†, and tungsten steel electrodes with 4 mm. spark gap, an exposure of 0·5 sec. suffices to give workable blackening of the photographic plate at wave-lengths from 4600 to 2100 Å. The accuracy of matching of spectra thus produced has been found by us to correspond to a density-difference of 0·01 in the absorbing substance‡. From this we find that for a measured density represented by 1, with exposure-time 5 sec., the limit of accuracy $\Delta D/D$ is 0·01. For double the density the figures are 50 sec. and 0·005 respectively.

(*b*) If the match points of a plate are determined by microphotometer instead of by eye the sensitivity is increased a number of times. At any point, the eye will in general perceive a match over a small range of wave-lengths. If the gradient of the absorption curve at the point is not too great there will be a number of lines in this range, and the microphotometer will find a match on only one (say) of these. In this way it has been found possible[*] to increase the accuracy of matching by *thirty times*[†]. In any case where there are insufficient lines for the microphotometer to match on any one line, it may be possible by direct interpolation to determine a point of match between two adjacent lines.

---

* As described by F. Twyman and C. S. Hitchen, *Proc. R. S.* A, **133**, 74 (1931), but without inductance in the spark circuit.

† Ilford panchromatic half-tone with developer No. 2 on the list on p. 659.

‡ With such photometric apparatus as that described by F. Twyman, *Trans. Opt. Soc.* **33**, 9 (1931–32).

(*c*) Direct measurement by objective photometer, using the optimum density (see p. 653). The sensitivity is limited by the amount of light which gets through the spectrometer. It may be necessary to open the slits to obtain sufficient light (see p. 647). It has been stated[‡] that under favourable conditions the sensitivity may be 10^2 times that of the photographic method in the determination of an extinction coefficient. The method is very much slower than the photographic, and must therefore be looked upon as supplementary to this latter.

There is probably a greater variation of sensitivity between different types of photo-electric instruments than of photographic instruments, and the most important limiting factor in the former is the method of measuring currents. There is probably little to choose in this respect between electrometer methods and valve amplification. With the recently developed "electrometer valves" the valve methods can probably be raised to a further degree of sensitivity than the electrometer methods, but up to the limits of their sensitivity electrometer methods are easier to use.

Measurements in the visible region. In the visible region visual, photographic and photo-electric methods are available, and the choice of a method depends on what accuracy is required, whether time is limited, and the nature of the absorption curve to be measured.

The visual method is the one most usually employed. With polarization spectrophotometers it is possible to make accurate readings up to densities of nearly 2·0 with forms obeying a $\tan^2$ law, or somewhat higher with a $\tan^4$ law.

The photographic method is often quicker. Moreover the whole of the spectrum may be studied on one plate. Reference to p. 653 will show that with the recommended Ilford half-tone plate the accuracy of measurement with the Spekker photometer is about 0·01 in dD/D.

As regards the time required: for measurements at a number of wave-lengths to obtain a complete curve, the photographic method is quicker than a photo-electric measurement when readings have to be obtained and plotted wave-length by wave-length. The photo-electric cell, however, lends itself to automatic reading of spectrophotometric curves. So far as we know this has only been performed in the visible region[§], but there is no reason why it should be so limited. This is the next most rapid method of spectrophotometry available, as about half a minute is sufficient to produce a complete curve in the visible region. The sensitivity is found to be limited by the finite thickness of the recording line, among other factors. It is a type of instrument which is extremely useful in industry for comparison, but presents great difficulties if absolute accuracy is sought.

---

[*] The microphotometer employed will be described shortly in another paper.

[†] The figures can be regarded as representing an increase of sensitivity but not necessarily of absolute accuracy, which latter will depend on the uniformity of cells, sector plates, etc.

[‡] H. von Halban and J. Eisenbrand, *Proc. R. S.* A, **116**, 162 (1927).

[§] A. C. Hardy, *J. Opt. Soc. Am.* **18**, 97, 165 (1929).

With a visual instrument a number of readings must be taken at each wave-length in order to obtain a mean result of high accuracy. This makes the method more lengthy, but the accuracy is greater than is often obtained by the photographic method.

Measurements in the infra-red. Photographic and photo-electric methods can be applied to the near infra-red up to about 1μ, but in general the thermopile or radiometer are used. The thermopile is most used nowadays. The Müller thermopile is a recent development with a very much greater sensitivity than the established types. It has been found by the present writers to be about 7 times as sensitive as the most sensitive other thermopile with which they are acquainted, and being enclosed it does not suffer much from unsteadiness.

§ 5. THE CHARACTERIZATION OF A RADIATION, SPECTROPHOTOMETRY IN CONNEXION WITH COLOUR, AND THE COMPARISON OF LIGHT-SOURCES

The problems relating to the spectrophotometric comparison of light-sources, including of course sources provided with filters, are in some respects similar to the preceding; but the ensuing paragraph will serve to emphasize points that require special consideration in this type of measurement.

We are now interested in the ratio of the intensities of two radiations, instead of, as in the previous sections, the logarithm of this ratio; and it is now $\Delta I/I$ that defines the sensitivity, where ΔI is the smallest detectable change in the light-intensity I. It should be repeated that within limits, $\Delta I/I$ for the eye and photographic plate is independent of I.

$\frac{\Delta I}{I}$

It is most often the case that the radiations to be measured are continuous spectra in which the rate of change of intensity with wave-length is not so great as it may be in absorption measurements in connexion with chemistry. Thus the considerations which in absorption work call for large dispersion (see p. 647) do not often arise acutely in the work now in question*.

Fluctuations in brightness of a single light-source will not affect the spectrophotometric curve appreciably if they are small; if, however, a comparison between two different light-sources is in question, a curve being plotted wave-length by wave-length as with a visual or photo-electric instrument, any change in intensity of one source during the measurement will result in a curve whose shape is misleading.

Thus it is desirable in such measurements to have the source considerably more steady than it need be in actual use. In the case of electric lamps this result must be achieved by using a very steady electric source such as a battery, or, with similar sources it is sufficient to connect both to the same electric supply.

---

* There is a kind of comparison of light-sources which lies outside the intended scope of this paper, namely, the comparison of line spectra, which forms the basis of spectrum analysis. In this of course the dispersion must suffice to separate the lines of the metals which are sought.

Photographed pairs of spectra examined visually or by microphotometer. As has already been seen, the probable error $\Delta I/I$ is independent of the exposure provided the plate be neither under nor over-exposed. To secure highest accuracy the most suitable type of plate is, as before, one with a large γ; with the plate recommended on p. 649 the limit of accuracy $\Delta I/I$ is equal to the limit of discernible density difference 0·01 divided by $\log_{10} e$. That is, an intensity can be determined with this plate with an error of 0·01/0·43 or 2·3 per cent.

It may be pointed out that in quantitative spectrum analysis by emission spectra, for a given method of exciting the spectrum of a given substance, the intensity of a line due to a metallic element is often approximately proportional to the percentage of the element present*, provided that the line is not subject to reversal. One might therefore expect to obtain an accuracy of about 2·3 per cent in the estimation of such an element. So far such accuracy has not been obtained. This may partly be due to limiting accuracy not having been sought, but we attribute it chiefly to the difficulty of running an arc or spark on two separate occasions in such a manner as to give radiations of identical character. Such a constancy would be strange; it is not likely that the various metallic vapours in the arc or spark gap will be present in the same proportions on the different occasions, nor that the electrical conditions of excitation within the gap will remain constant. The selection of Gerlach's homologous line pairs† is a step towards avoiding the latter source of error.

No doubt it was with applications to colorimetry in mind that Guild so strongly disfavoured that class of instrument (which we designate the "first type") in which "the observer views through the eyepiece of a spectroscope two adjacent spectra, one above the other, isolating a small wave-length range by means of adjustable shutters in the eyepiece‡," and favours a second type in which "the observer looks through a slit situated in the plane of the spectra...and sees a suitably divided field"‡ of the dimensions generally accepted for photometric work §. The essential difference between the two types is that in the first the available light is concentrated into a slit image which constitutes the photometric field, while in the second type the available light is distributed over a relatively large photometric field.

It must be remembered that for large densities and with slits narrow enough to give a sufficiently pure spectrum the amount of light available is very small, and the field of view will in no case be very bright. In each type mentioned there are two opposing features which respectively increase and decrease the accuracy of reading attainable. Thus the greater brightness of the field in the first type, as compared with that in the second, enhances the accuracy of readings. On the other hand, for a constant brightness the standard field of the second type allows of more accurate reading than the narrow-slit field of the first type.

---

* F. Twyman and A. Harvey, *J. Iron and Steel Inst.* No. 11, 397 (1932); F. Twyman and C. S. Hitchen, *Proc. R. S.* A, **133**, 87 (1931).

† F. Twyman and A. Harvey, *loc. cit.* p. 399.

‡ J. Guild, *Proc. Opt. Convention* 1926, pp. 21, 22.

§ A field of 2° has been recommended by Ives for flicker photometry and by Guild for colorimetry, *ibid*, pp. 36, 72.

It is not obvious at first sight which of the two factors has the greatest effect and it is a matter of experiment to determine which of the two types will be better.

A Hilger-Nutting spectrophotometer (an instrument of the first type) is easily converted into one of the second type by covering one-half of the object-glass of the spectrometer telescope with a prism of small angle, about 9′, so that spectra normally closely adjacent become accurately superposed. On then removing the eyepiece and viewing the object-glass through the slit one sees the type of field used in the second class. In this way a very direct comparison of the two types was made. With various widths of the collimator slit and a telescope slit-width of 5 Å. at the *D* lines readings were made on a density of about 1·7. At a wave-length of 5890 Å. it was found possible for a skilled observer with great concentration* to take readings having a mean error of 0·03 in density with a collimator-slit opening of 4 Å. By means of the slit field, however, it was possible to get readings with a mean error of less than half of this with a slightly smaller width of collimator slit (3 Å. at the *D* lines). Moreover it was possible to take these readings with far greater comfort, an important factor in taking a large number of readings.

Apart from this, in the second type there will be a tendency to obtain sufficient brightness by opening the telescope slit; and the use of an eyepiece to observe and limit this width according to the gradient of absorption is an additional adjustment and one liable to be overlooked in routine work by some of those who have to use spectrophotometers. Thus, as the result of experiment, it would seem that for accurate measurements of high density spectrophotometers using a slit field are not merely as good as the other type, but definitely preferable to it.

Photo-electric measurements. It appears that for measurements of this character photo-electric methods are peculiarly appropriate, for in these I is a constant so that by making I very large we can make the error in measuring $\Delta I/I$ very small.

Choice of a method for a particular purpose in this section. In comparison of light-sources which are liable to be unsteady a photographic method is preferable, so that exposure for the whole spectral range is made at the same time. We can then derive from the measurements a curve of comparison of the light-sources which is true at the time of taking the photograph. If comparison is made point by point, any individual measurements may be subject to a variation from the average value peculiar to the moment at which the reading was taken. If, however, a more sensitive photo-electric arrangement is available, it will be of advantage to use it provided that the variation of the source can be kept less than is detectable with the photographic plate.

The choice of a suitable method for other purposes in this section will depend on considerations similar to those already elaborated at the end of § 2, to which reference should be made.

---

* The difficulties of observing this field are threefold: (1) the very small brightness; (2) the very narrow eye-pupil necessitates keeping the eye very steady; (3) some diffusion of the image arises owing to the very narrow eye-pupil.

§ 6. ACKNOWLEDGMENTS

The thanks of the authors are due to Dr Simeon, Mr Perry, Mr Follett, Mr Spencer and Dr Harvey of the staff of Adam Hilger, Ltd., for help in connexion with various points which arose in the writing of this paper.

APPENDIX

Table 1. γ values for various plates, obtained by using the developers 1, 2, 3 described below at 65° F.

Time of development (minutes at 65° F.)	γ values obtained for light of the quality specified			
	White light; colour temperature 2360° K. (vacuum lamp)	White light (2360° K.) screened by filters		
		Tricolour blue 3900–5150 Å.	Tricolour green 4800–6100 Å.	Tricolour red 5800 Å.–red end
	Ilford Panchromatic Half-tone Developer no. 2: caustic potash, hydroquinone			
2	6–7	5–6	6–7	8·5–9·5
3	7–8	6–7	8–9	9–10
	Ilford Rapid Process Panchromatic Developer no. 2: caustic potash, hydroquinone			
2	3–4	2·5–3·5	2–3	3–4
3	4–5	2·5–4	3–4	4–5
	Wellington Soft Spectrum Developer no. 1: metol, hydroquinone			
5	1–1·5	0·6–0·9	1–1·5	1–1·5
7½	1·25–1·75	0·80–1·2	1·25–1·75	1·25–1·75
	Ilford Hypersensitive Panchromatic Developer no. 1: metol, hydroquinone			
5	0·5–0·7	0·4–0·6	0·5–0·7	0·5–0·7
7½	0·6–0·8	0·5–0·7	0·6–0·8	0·6–0·8
	Wellington Anti-Screen Developer no. 1: metol, hydroquinone γ obtained on exposure to light of mean noon sunlight quality (Washington)			
5	1·25–1·75			
	1·50–2·0			
	Ilford Special Lantern plate Developer no. 3 Exposure to light from unscreened vacuum lamp at 2360° K.			
2	1·75–2·0			
3	2·00–2·5			

We have to thank Ilford, Ltd., for very kindly supplying the information contained in the above table.

Table 2. Methods of development

(1) Metol, hydroquinone.

Metol	2 gm.
Sodium sulphite (crystals)	100 gm.
Hydroquinone	8 gm.
Sodium carbonate (crystals)	100 gm.
Potassium bromide (10 per cent solution)	8 cm^3.
Water up to	1000 cm^3.

For use take 1 part with 2 parts of water.

(2) Caustic potash, hydroquinone.

A.	Caustic potash	50 gm.
	Water up to	1000 cm^3.
B.	Hydroquinone	25 gm.
	Potassium metabisulphite	25 gm.
	Potassium bromide	25 gm.
	Water up to	1000 cm^3.

For use take equal amounts of A and B.

(3) Developer for black tone (rapid) lantern plates.

A.	Hydroquinone	9 gm.
	Sodium sulphite (crystals)	50 gm.
	Water up to	500 cm^3.
B.	Caustic soda	5 gm.
	Potassium bromide	2 gm.
	Water up to	500 cm^3.

For use take equal amounts of A and B.

DISCUSSION

Mr J. Guild: The authors have drawn explicit attention to several important considerations which, while familiar enough to those who have had to give special attention to these problems, are apt to be overlooked by those who merely *use* spectrophotometers, and sometimes also, though less excusably, by those who design them.

I have three minor criticisms to offer; two of a general character and one of a specific character. The first is that although the authors are careful to draw attention in several places to the important distinction between precision and accuracy, their specific conclusions regarding the potentialities of different methods are based entirely on criteria of precision. Nowadays the experienced experimenter in all branches of experimental science attaches much less importance to precision than was attached in earlier days, when all apparatus was relatively crude and its precision was the governing factor in determining its utility. Now, however, Messrs Hilger and other similarly progressive instrument makers provide us with such sensitive apparatus of all kinds that the reproducibility of the results we can obtain with them is no longer a useful criterion of the value of these results, which is generally determined by other considerations altogether. These considerations are not so readily reducible to formulae, and so are usually ignored in any formal treatment of the merits of equipment or methods; but to ignore them is dangerous. No experienced worker ignores them in considering the equipment or methods which he will use himself, and so he is guilty of suppressing something which he knows to be important if he ignores them in instructing others.

If two instruments are to be used under practically identical conditions, all the essential operations involved in their use being the same in each case, then the more precise instrument is the better one for the job in question; but if the use of one instead of the other involves essential alterations in the conditions of experiment, so that factors have to be taken into account in one case which do not have to be considered in the other, then a judgment based on relative precision may be entirely misleading.

This is well illustrated by the present state of affairs in this very subject of spectrophotometry. The visual method is among the least precise of available methods, yet, curiously enough, at the present time it is the method on which most reliance is placed by the spectrophotometrists of the various National Laboratories, despite the fact that alternative methods of much greater precision are available in most of these institutions. This predilection is based on miscellaneous experience, and in its justification can be adduced the indisputable fact that there are far more spectrophotometric data, of verified high accuracy, for the range of wave-lengths within which the visual methods are applicable than for the ultra-violet and infra-red regions where other methods must perforce be employed.

This is not necessarily a permanent state of affairs. It is the aim of most spectrophotometrists to bring physical methods to a degree of reliability which will enable them to supersede visual methods altogether, but this has not yet been done, despite the extravagant claims, based on sensitivity, put forward by various inventors of physical spectrophotometers; and the present state of affairs, which we all hope will become a past state in the near future, shows of how little use precision is as a guide to the best available method. The photographic method, which ranks fairly high if we take as criterion the sensitivity figures given in this paper, ranks very low in the estimation of spectrophotometrists. In the National Physical Laboratory we never use it except as a last resort in cases where we cannot apply any other method, as, for instance, when light-sources of an unsteady character are involved. While I cannot speak with certainty for others on this point, I should be very greatly surprised if this were not also the status of the method in other standardizing institutions.

The second general criticism which I have to offer is that by drawing a distinction between the problems of measuring density and measuring transmission the authors may lead an unwary reader into the pitfall of confusing arithmetic with physics. The process of spectrophotometry is always the measurement of relative quantities of light, not darkness. In the case of a slab of material the quantity measured is transmission, never anything else. The problems of measurement are not affected when, for some purpose, it becomes convenient to invert the answer and take its logarithm. The method, whatever it may be, which for a given specimen will give the greatest accuracy in the transmission at a given wave-length is clearly giving the most accurate information about the specimen, whatever function of the result we are interested in. I am quite certain the authors themselves will agree with this; but I can easily imagine a reader concluding from the paper that for a given specimen the best method of spectrophotometry to use depends on whether he is interested in the light which the specimen lets through or the light which it stops.

Although it is not quite relevant to this paper, which is not concerned with nomenclature, I should like to deprecate most strongly the habit of physical chemists and others of inventing new derived magnitudes, such as density, in order to convert multiplication into addition. It is quite possible, after all, to use logarithms as a legitimate aid to arithmetic without inventing a new magnitude to be represented by the logarithms of the magnitudes with which we are really concerned. Our terminology should be kept in as close correspondence as possible with the physical magnitudes actually handled in our experiments.

The third point to which I wish to refer is the only one on which I would differ from the authors on a question of fact. In § 5 reference is made to certain views expressed by me on the merits of two types of visual spectrophotometer. The authors find themselves in agreement with these views only as regards cases where comparatively transparent specimens are involved so that there is plenty of light; and, with characteristic courtesy, express the belief that I had only such cases in mind. This is not so: I intended the opinion in question to be as general and sweeping as possible, and if it can be shown to be wrong in any circumstances whatever then I was just wrong. I am still of the opinion, however, that instruments of the "second type," giving a Maxwellian view, are superior to those of the "first type" as exemplified in the Nutting spectrophotometer in all circumstances, despite the evidence which the authors adduce to show that when the available intensity is very low the latter type is better. I do not consider that a fair comparison can be made merely by adapting an instrument designed for use in one way so that it can be used temporarily in another way and then regarding its behaviour as typical of the merits of these two ways. The question is how instruments, properly designed to obtain the best possible results by each method, compare with one another. In so far as I am capable of interpreting performances expressed in terms of density, there is no doubt at all that with the apparatus used at the National Physical Laboratory a precision very much superior to the figures obtained in the authors' tests is obtained with very much denser specimens than those mentioned. As a matter of fact, it was the inadequacy of the Hilger-Nutting spectrophotometer for use when illumination is low—as it always is at the ends of the spectrum, however transparent the specimen under test may be—which led me to make the categorical statement referred to.

A further disadvantage of this type of instrument is that in cases where the transmission curve is sloping very steeply, the mode of subjective integration which is operative within the range of wave-lengths comprised by the telescope slit is unknown, and the necessary slit-width correction cannot be evaluated unambiguously. With the Maxwellian view, on the other hand, the slit-width correction can always be quite definitely computed.

AUTHORS' reply. We have reviewed our argument in the light of Mr Guild's criticisms, and although we are in general agreement with what is said, we still find no escape from our conclusions. Two specific points that are raised appear to call for further comment. The term "density" is employed as a measure of absorption. Absorption is not merely a derived magnitude but a phenomenon of direct physical significance and of considerable importance in some applications of spectrophotometry. We do not think Mr Guild would advocate also the abolition of the term "absorption," and it is clear that, when the emphasis is on this aspect of the measurements, to refer shortly to "density" saves considerable circumlocution.

In regard to the comments on the accuracy attainable, it must not, of course, be forgotten that the Hilger-Nutting spectrophotometer, in common with other instruments, has improved considerably since the date of Mr Guild's first experience with it.

The accuracy obtained by Mr Guild is surprisingly good and seems better than what is generally considered possible, considering the known limitations of the human eye in the discrimination of intensity.

We value the remarks of Mr Guild on this subject and are very pleased to have them associated with our paper for the benefit of those interested in present-day developments in spectrophotometry.

535.88

THE VISIBILITY OF OBJECTS IN A SEARCHLIGHT BEAM

By W. M. HAMPTON, Ph.D., B.Sc. (Lond.), F.Inst.P.

Received January 29, 1933. *Read June* 2, 1933

ABSTRACT. The paper is almost entirely mathematical, and calculates the effect on the visibility of an object, illuminated by a projector, of the scattering and absorption of the light by the atmosphere. The discussion is divided into three parts dealing separately with the light reflected from the object from the incident beam, with the brightness of the atmospheric background due to scattered light, and of the conditions of visibility as functions of the two previous quantities. Numerical solutions of the equations are given and range curves are drawn for objects of different sizes and different reflecting powers and for sources of varying intensity.

---

§ 1. INTRODUCTION

It is well known that the range of a searchlight is limited by two main factors. The first is the attenuation of the illumination due to scattering and absorption in the atmosphere and to the spread of the beam, which varies inversely as the square of the distance between source and object. The second is the background of light due to the flux scattered by the atmosphere from the beam of the searchlight itself. Attempts have been made to calculate these two effects from fundamental considerations, but the author is unaware of any publication which has carried the investigation to the stage of drawing (intensity, range) curves. This is what is now attempted on the basis of certain definite assumptions.

The subject of discussion is divided into three main parts: (1) the light reflected from the object from the incident beam; (2) the brightness of the atmospheric background due to light scattered from the incident beam; (3) the conditions of visibility as functions of (1) and (2) above.

Each of these sections being taken in turn, the assumptions involved may be stated. In (1) it is assumed that a reflecting surface which subtends an angle so small as to be below the limit of resolution denotes its presence only by the light reflected from it, and that the effect on the eye is the same for such a secondary source as it is for a primary source of the same intensity. This is probably justified. In (2) it is assumed that no light is absorbed by the atmosphere but that all the light that does not reach the spherical surface which includes the object and has the source as centre is scattered. If any light is absorbed, as is certainly the case in practice, the scattered light will be correspondingly reduced and the background brightness diminished. The further simplifying assumption is made that the scattering is uniform in all directions. Rocard* calculates that the forward scattering is some ten times the backward scattering, so that this assumption also tends to make the background brightness higher than it should be with the result that the range, as calculated later, tends to be low. Thus, it is probable that the calculated range figures deduced are minima. In (3), for simplicity, an empirical relation between the minimum illumination needed for conspicuity and the background brightness is taken. It can only be stated that the values given by this equation are in general agreement with data available in this country and are, of course, justified by the results obtained by the authors of the expression.

§2. THE LIGHT REFLECTED FROM THE OBJECT

In figure 1 let B be the object in the beam of the projector placed at A and let an observer be placed at C.

R Let R be the range AB of the light;
δ δ the distance AC between projector and observer;
I_0 I_0 the initial luminous intensity in the beam;
I I the effective intensity at distance R; and
κ κ the fraction of light absorbed and scattered per unit distance.

Then
$$I = I_0 e^{-\kappa R} \qquad \text{......(1).}$$

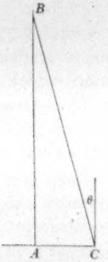


Figure 1.

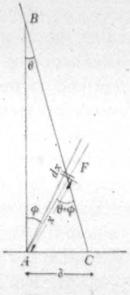


Figure 2.

ρ The illumination on the object at B is I/R^2, and if ρ is the diffuse reflection factor of the object (assumed to be perfectly diffusing but grey) its brightness is given by
$$\rho I_0 e^{-\kappa R}/\pi R^2.$$

b Since the object as seen from C has to send its reflected light through a distance BC, its apparent brightness b is then given by
$$b = \rho I_0 e^{-\kappa(R+BC)}/\pi R^2 = \rho I_0 e^{-\kappa R(1+\sec\theta)}/\pi R^2$$
$$\fallingdotseq \rho I_0 e^{-2\kappa R}/\pi R^2 \quad \text{when } \theta \text{ is small} \qquad \text{......(2)†.}$$

---

* Rocard, *Revue d'Optique*, No. 5, p. 202 (1932).
† See A. Blondel, *Ill. Eng.* **8**, 87 (1915).

Now the brightness of an object is only of interest if the object is large, that is to say, in practice, if it subtends an angle greater than, say, 2° at the eye of the observer. If the subtended angle is small, the important property is the total light-intensity in the specified direction. Thus, let a be the area of the object, assumed as square for simplicity. a

Then the intensity i in the observer's direction is given by i

$$i=\frac{a\rho I_0 \cos\theta \,.\, e^{-\kappa R}}{\pi R^2},$$

and the illumination e_1 produced at the observer's eye is given by e_1

$$e_1=ie^{-\kappa(BC)}/(BC)^2;$$

or since $BC=R\sec\theta$,

$$e_1=\frac{a\rho\cos^3\theta \,.\, e^{-\kappa R(1+\sec\theta)}}{\pi R^4},$$

or when θ is small,

$$e_1=\frac{a\rho I_0 e^{-2\kappa R}}{\pi R^4} \qquad \text{......(3).}$$

If the object subtends a constant angle ψ at the observer's eye ψ

$$e_1=\frac{\psi\rho I_0\cos\theta \,.\, e^{-\kappa R(1+\sec\theta)}}{\pi R^2},$$

or

$$e_1 \doteqdot \frac{\psi\rho I_0 e^{-2\kappa R}}{\pi R^2} \quad \text{when } \theta \text{ is small.} \qquad \text{......(4).}$$

§ 3. THE BRIGHTNESS OF THE ATMOSPHERIC BACKGROUND DUE TO SCATTERED LIGHT

In figure 2, consider an elementary volume of air at F, of unit area and thickness dx, distant x from A. The light falling on this unit is $I_\phi e^{-\kappa x}$ and the light scattered in the thickness dx is x

$$\kappa I_\phi e^{-\kappa x} x^{-2}\,dx.$$

Since this is assumed to be scattered uniformly, the brightness in any direction is $(\kappa/4\pi)\,I_\phi e^{-\kappa x}x^{-2}\,dx$. The thickness of the layer as seen from C is $dx\sec(\theta+\phi)$, and the apparent brightness is

$$(\kappa/4\pi)\,I_\phi e^{-\kappa(x+FC)}\,x^{-2}\sec(\theta+\phi)\,dx \qquad \text{......(5).}$$

From the figure,

$$R\sin\theta=x\sin(\theta+\phi)$$

and

$$R\tan\theta=\delta,$$

whence

$$\delta=x\sin(\theta+\phi)\sec\theta.$$

Also

$$FC=BC-BF=\frac{\delta}{\sin\theta}-\frac{R\sin\phi}{\sin(\theta+\phi)},$$

whence, on reduction, $x+FC=\delta(\cos\theta+\cos\phi)\operatorname{cosec}(\theta+\phi)$.

Also $x=\delta\cos\theta\operatorname{cosec}(\theta+\phi)$ and $dx=\delta\cos\theta\cos(\theta+\phi)\operatorname{cosec}^2(\theta+\phi)\,d\phi$.

Substitution in (5) gives

$$(\kappa/4\pi\delta)\, I_\phi e^{-\kappa\delta(\cos\theta+\cos\phi)\operatorname{cosec}(\theta+\phi)} \sec\theta\, d\phi;$$

or the total brightness

B

$$B=\frac{\kappa}{4\pi\delta\cos\theta}\int_{-\theta}^{\pi/2} I_\phi e^{-\kappa\delta(\cos\theta+\cos\phi)\operatorname{cosec}(\theta+\phi)}\, d\phi \qquad \text{......(6)[*].}$$

For the case of a concentrated beam, such as that of a searchlight, where the ϕ_1 angle of the beam may be taken as $\pm\phi_1$ and I_ϕ may be taken to a first approximation as constant over this angle, and θ is small:

$$B=\frac{\kappa I_0}{4\pi\delta}\int_{\substack{-\phi_1\\ \text{or } -\theta}}^{\phi_1} e^{-2\kappa\delta/(\theta+\phi)}\, d\phi \qquad \text{......(7).}$$

§ 4. THE VISIBILITY OF OBJECTS IN THE BEAM

For objects whose angular subtense approximates to 2°, the visibility is governed by the ratio b/B which becomes in effect the Fechner fraction. This has been shown to vary with B[†], but since a 2° object at 5000 ft. would be 170 ft. long or 29,000 ft^2 in area, it is clearly not a problem which frequently arises.

If the Fechner fraction were truly constant the range of a searchlight would be independent of its intensity since (2) ÷ (7) is independent of I_0. Thus,

$$\frac{\rho I_0 e^{-2\kappa R}}{\pi R^2}\Big/\frac{\kappa I_0}{4\pi}\int e^{-2\kappa\delta/(\theta+\phi)}\, d\phi=\frac{4\rho\delta e^{-2\kappa R}}{\kappa R^2\int e^{-2\kappa\delta/(\theta+\phi)}\, d\phi}=\Phi \qquad \text{......(8),}$$

where Φ is Fechner's fraction.

This fraction is, however, constant over a considerable range of background brightness, and for this condition R may be computed from (8).

The more important practical case is that of smaller sources than would subtend 2° at the observer's eye. Langmuir and Westendorp[‡] have given an empirical formula, which is sufficiently accurate over the range required, indicating the relation between the background brightness and the illumination produced at the observer's eye by the source needed for adequate conspicuity. The formula is

$$e_1=1{\cdot}08\times10^{-7}\sqrt{B} \qquad \text{......(9),}$$

where e_1 and B have the meanings already allocated. e_1 is sufficient for foveal vision when B exceeds about 10^{-3} candles/ft^2.

Thus, when θ is small, by combination of (3), (7) and (9)

$$\frac{a\rho I_0 e^{-2\kappa R}}{\pi R^4}=1{\cdot}08\times10^{-7}\sqrt{\left\{\frac{\kappa I_0}{4\pi\delta}\int_{\substack{-\phi_1\\ \text{or } -\theta}}^{\phi_1} e^{-2\kappa\delta(\theta+\phi)}\, d\phi\right\}},$$

whence

$$\frac{e^{-2\kappa R}}{R^4}=\frac{0{\cdot}54\times10^{-7}}{a\rho}\sqrt{\left\{\frac{\kappa\pi}{\delta I_0}\int_{\substack{-\phi_1\\ \text{or } -\theta}}^{\phi_1} e^{-2\kappa\delta/(\theta+\phi)}\, d\phi\right\}} \qquad \text{......(10),}$$

from which R may be computed.

---

[*] For a similar expression, see Rocard, *loc. cit.* p. 207.

[†] W. S. Stiles, "The effect of glare on the brightness difference threshold," *Dept. Sci. Ind. Res.* Paper no. 8 (p. 23).

[‡] *Physics*, **1**, 273–317 (1931).

§ 5. NUMERICAL SOLUTIONS

For these solutions δ has been taken as 100 ft.;
ϕ_1 as 0·020 radians; and
ρ as 1·0.

Case 1. $\kappa = 0$, i.e. the atmosphere is perfectly clear.

It follows that $B = 0$ and (7) and (10) are therefore useless. It is known, however, that when $B = 0$, $e_1 = 0{\cdot}54 \times 10^{-8}$ foot-candles.

Then from (3)

$$R^4 = aI_0/0{\cdot}54 \times 10^{-8}\pi.$$

Values of R from this for various values of I_0 and a are given in table 1.

Table 1.

I_0 (candles × 10^6)	R (hundreds of feet)			
	$a = 200$	$a = 100$	$a = 50$	$a = 25$
100	329	277	233	196
200	390	328	276	232
400	465	392	330	278
600	514	433	364	307
800	554	466	392	330
1000	583	491	413	347
1500	645	543	457	384

Case 2. $\kappa = 0{\cdot}0000095$, giving 95 per cent transmission per mile as in normal clear weather.

The values of the integral $\dfrac{1}{\delta}\displaystyle\int_{\substack{-\phi_1\\ \text{or } -\theta}}^{\phi_1} e^{-2\kappa\delta/(\theta+\phi)}\,d\phi$ in equations (7) and (10), which we shall denote by A_1, have been evaluated graphically and are shown in table 2. A_1
In this process $-\phi_1$ or $-\theta$, whichever is the smaller, is taken as the lower limit.

Table 2.

R (hundreds of feet)	θ (radians)	Limits of integral (radians)	Values of integral A_1
10	0·100	0·020 to − 0·020	0·000391
20	0·050	0·020 to − 0·020	0·000383
30	0·033	0·020 to − 0·020	0·000362
40	0·025	0·020 to − 0·020	0·000343
50	0·020	0·020 to − 0·020	0·000327
100	0·010	0·020 to − 0·010	0·000233
150	0·007	0·020 to − 0·007	0·000200
200	0·0050	0·020 to − 0·0050	0·000181
300	0·0033	0·020 to − 0·0033	0·000170
400	0·0025	0·020 to − 0·0025	0·000165
500	0·0020	0·020 to − 0·0020	0·000162
1000	0·0010	0·020 to − 0·0010	0·000155
2000	0·0005	0·020 to − 0·0005	0·000150
∞	nil	0·020 to ∞ nil	0·000141

Then the background brightness in candles/ft.^{2} is given by 0·0000095 $A_1 I_0/12\cdot56$ for various values of R and I_0. These are shown in table 3.

Table 3.

I_0 (candles × 10^8)	B (candles/ft.^{2})	
	$R = 1000$	$R = \infty$
1	0·028	0·010
2	0·059	0·021
4	0·12	0·042
6	0·18	0·063
8	0·23	0·085
10	0·29	0·105
15	0·44	0·160

Thus for this weather condition and when I_0 is between 100 and 1500 million candles, the background brightness only varies from 0·010 to 0·440 candles/ft.^{2} The value of the Fechner fraction varies from 0·8 to 1·2 per cent.

For small sources R is given by the expression

$$\frac{e^{-2\kappa R}}{R^4} = \frac{1\cdot08 \times 10^{-7}}{2a}\sqrt{\frac{0\cdot0000095\pi A_1}{I_0}} = 2\cdot95 \times 10^{-10}\sqrt{\frac{A_1}{I_0 a^2}}$$

where A_1 is given above.

Graphical solution only is possible and figure 3 gives values of the left-hand side for various values of R. From this curve are obtained the solutions shown in table 4.

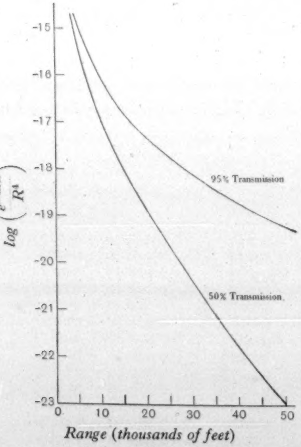


Figure 3.

Table 4.

I_0 (candles $\times 10^8$)	R (hundreds of feet)			
	$a = 200$	$a = 100$	$a = 50$	$a = 25$
1	250	210	180	150
2	270	232	195	165
4	290	250	210	180
8	313	265	230	190
15	336	290	250	210

Case 3. Transmission 50 per cent per mile; $\kappa = 0{\cdot}000095$.

Table 5. Values of integral A_2, viz. $\dfrac{1}{\delta}\displaystyle\int_{\substack{-\phi_1 \\ \text{or } -\theta}}^{\phi_1} e^{-2\kappa\delta/(\theta+\phi)}\, d\phi$.

R (hundreds of feet)	A_2	R (hundreds of feet)	A_2
10	0·000327	200	0·000050
20	0·000276	300	0·000040
30	0·000215	400	0·000039
40	0·000166	500	0·000038
50	0·000131	1000	0·000035
100	0·000075	2000	0·000032
150	0·000055	∞	0·0000309

The values of the background brightness vary from 3·7 candles/ft.² (when $R = 1000$, $I_0 = 15 \times 10^8$) to 0·047 candles/ft.² (when $R = \infty$, $I_0 = 10^8$).

For small sources
$$e^{-2\kappa R}/R^4 = 2{\cdot}95 \times 10^{-9}\sqrt{(A_2/a^2 I_0)}.$$

Table 6.

I_0 (candles $\times 10^8$)	R (hundreds of feet)			
	$a = 200$	$a = 100$	$a = 50$	$a = 25$
1	100	90	80	70
2	110	100	85	75
4	120	105	90	80
8	130	110	95	85
15	135	115	100	90

Any change in a and ρ give corresponding effects on the range, i.e. halving the area has the same effect as halving the reflecting power. This is illustrated in table 7, where $I_0 = 2 \times 10^8$ and the atmospheric transmission is 95 per cent.

Table 7.

ρ	R (hundreds of feet)			
	$a = 200$	$a = 100$	$a = 50$	$a = 25$
1·0	270	232	195	165
0·5	232	195	165	137
0·25	195	165	137	117
0·125	165	137	127	100

Table 8. $I_0 = 200 \times 10^6$; the atmospheric transmission is 50 per cent.

ρ	R (hundreds of feet)			
	$a = 200$	$a = 100$	$a = 50$	$a = 25$
1·0	110	100	90	80
0·5	100	90	80	67
0·25	90	80	67	60
0·125	80	67	60	52

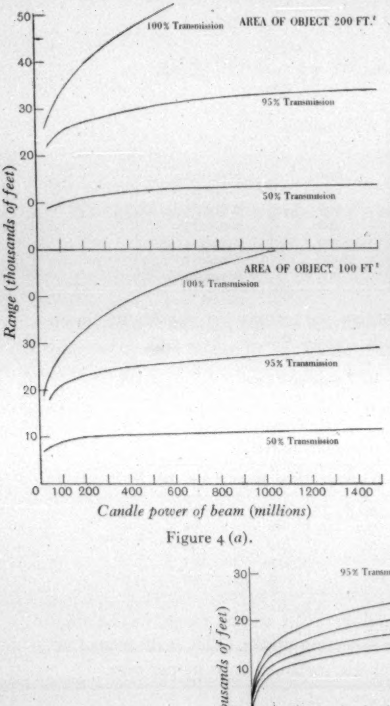


Figure 4 (a).

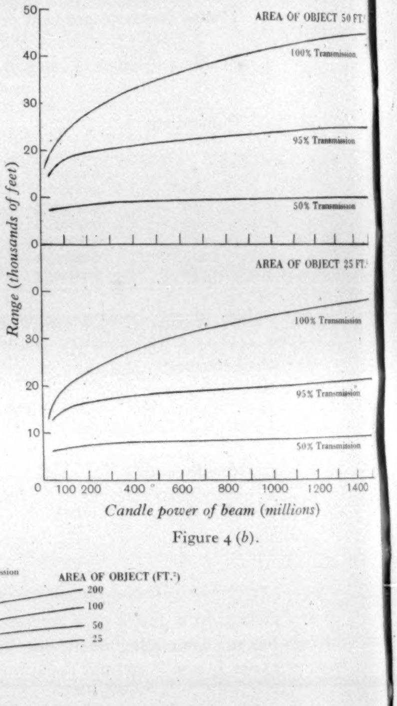


Figure 4 (b).

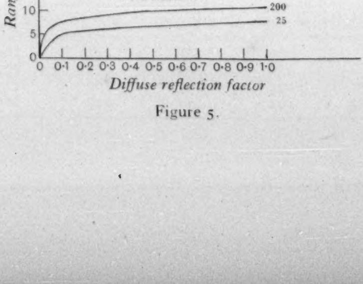


Figure 5.

§ 6. CONCLUSIONS

Increase in intensity has a decreasing effect on the range of the searchlight as the intensity increases. The range becomes more nearly independent of the intensity as the transmission of the atmosphere decreases. The range increases as the area of the object increases, though not proportionally, provided the object is sufficiently small to be considered as a point source.

DISCUSSION

Mr H. G. Bennett. The author's results agree fairly well as regards order of magnitude with some experimental results given by Messrs Sperry in a recent catalogue of optical equipment. The most striking difference between the two sets of results is at the lower beam-intensities. Messrs Sperry find that increases of intensity have a marked effect on range up to, say, 500 million c.p., whereas the author finds that the effect becomes much reduced above, say, 200 or 300 million c.p. Such differences are to be expected when it is realized that the conditions of experiment probably did not correspond with the hypotheses of the theory in a number of respects. This being so, it is remarkable that such near agreement at the higher intensities was obtained.

These considerations lead me to ask the author how much his results would have been affected had he taken other values for the threshold, the distribution of light in the beam, etc. Workers in visibility know only too well how small differences in the conditions may affect one's ability to see, and if the author would answer this question it would greatly help in the comparison of his theory with practical results.

Mr J. H. Awbery. I would refer to § 5 on "numerical solutions." Immediately below table 1 is the quantity A_1 or $\frac{1}{\delta}\int_{a}^{\phi_1} e^{-2\kappa\delta/(\theta+\phi)}\,d\phi$, which is stated to have been evaluated graphically. In general, I am convinced that numerical methods, such as Simpson's rule, give not only more accurate but also more rapid solutions to such problems. In this particular case, A_1 can be reduced to tabulated functions by taking $2\kappa\delta/(\theta+\phi)$ as a new variable. Then $A_1/2\kappa = [e^{-y}/y + Ei\,(-y)]$, taken between the limits $y = 2\kappa\delta/(\theta+\phi_1)$ and $2\kappa\delta/(\theta+\alpha)$. The *Ei* functions are tabulated in Jahnke and Emde's *Funktionentafeln*, p. 21*.

On the next page of the paper the equation $e^{-2\kappa R}/R^4 = CA_1^{\frac{1}{2}}/aI_0^{\frac{1}{2}}$ has to be solved for a number of values of a and I_0. When κ and δ are kept constant each side of the equation is a function of R only, since A_1 depends on that variable. From figure 3 it appears that the equation was solved by finding the intersections of the two curves representing them. This involves drawing a fresh curve to represent the right-hand side for each pair of values of a and I_0. A much less tedious process would have been to plot $e^{-2\kappa R}/R^4 A_1^{\frac{1}{2}}$, in which case only one curve would be needed.

---

* B. G. Teubner (Berlin, 1923).

The value of R would simply be read off opposite the value of $C/aI_0^{\frac{1}{2}}$. Incidentally, this equation shows that R is unchanged by any alteration of a and I_0 which leaves $I_0 a^2$ unaffected. This is only approximately so in table 4, as may be seen by comparing the entries in the line for $I_0 = 2$ with those in the next succeeding columns, for $I_0 = 8$. It may be worth remarking that if the integrations are more accurately carried out the numbers in table 4 are altered by less than 5 per cent (downwards).

AUTHOR's reply. I am obliged to Mr Awbery for his interest in my paper, especially as he was moved to recalculate so many of the figures. I was unaware of any tabulated functions which would assist in the necessary calculations, although I searched the tables of integrated functions which were known to me. I agree that the methods suggested by Mr Awbery yield useful results as he indicates, but it appeared simpler to me to make use of graphical integration.

In reply to Mr BENNETT: It was the general agreement of my calculated results with those published by Messrs Sperry that encouraged me to proceed with the presentation of this paper. I have not investigated the effect of variations in the threshold values of illumination on the ranges given, because the experimental (illumination, background-brightness) curve for the observer would have to be used to find how such changes affected the results. The same remark applies to the distribution of light in the beam. Given the polar curve of a searchlight, graphical or numerical integration would give the background-brightness from the equations provided, and I suggest that it is for others who have experimental range results to check up particular cases in order to confirm or reject the relatively simple theory I have put forward.

551.594.11 551.51.053.5

ON TWO METHODS OF IONOSPHERIC INVESTIGATION

By E. V. APPLETON, F.R.S., Halley Stewart Laboratory,
King's College, London

Received June 8, 1933. *Read July* 7, 1933

ABSTRACT. Two wireless methods of measuring upper-atmospheric ionization, both of which involve measurements of the equivalent height of reflection for a number of electric wave frequencies, are described. Different relations are expected and found to exist between the equivalent height and the frequency for the ordinary and extraordinary magneto-ionic components. From the examples chosen to illustrate the methods the following deductions and measurements concerning ionospheric characteristics are made. (*a*) Magneto-ionic double refraction is caused by region E; this shows, as was previously demonstrated in the case of region F, that free electrons are the effective electrical agents. (*b*) For daytime conditions, and more frequently in summer than in winter, evidence of the existence of a protuberance or "ledge" on region F is found, which most probably indicates that under direct solar influence this region is sometimes composite. Evidence of the existence of ionization between regions E and F ("intermediate region") has also occasionally been obtained at noon so that the whole ionospheric configuration may be regarded as a composite structure of four components. From the point of view of practical radio communication, however, it is sufficient to regard the ionosphere as divisible into two main regions, E and F, but where it is necessary to consider further the ionospheric fine structure it is proposed to name the four components, at successive increasing equivalent heights, regions E^{I}, E^{II}, F^{I} and F^{II}. Usually only regions E^{I} and F^{II} are of importance. (*c*) The rate of decay of region-F ionization during the night has been measured and found not to be explicable in terms of the simple law of recombination between ions and electrons. (*d*) Measurements have been made of the rate of production of electrons in region F during the period following sunrise.

§ 1. INTRODUCTION

In recent work on the exploration of the ionosphere by means of electric waves it has become increasingly clear that one of the most useful indices of ionospheric conditions is a curve exhibiting the equivalent height of reflection as a function of electric wave frequency. In the early experiments of 1925–8 the diurnal variation of the equivalent height of the reflecting region for a single mean frequency was studied, and it was such experiments which led to the recognition of the separate existence of an upper reflecting region situated above the Kennelly-Heaviside layer as well as the phenomenon of magneto-ionic splitting. But it has since been realized that work on a single frequency, useful though it has proved, is not likely to give us the maximum amount of information concerning ionospheric conditions, and that the extra amount of effort required to make hourly series of measurements on as many frequencies as possible is well worth while.

P'

t

f

For measurements made by both frequency-change and group-retardation methods it has been shown that the results in each case give us the value of P', the equivalent path of the atmospheric or space-waves. The type of record most frequently obtained in ionospheric observations is therefore that exhibiting the relation between P' and the time t. I shall refer to this as a (P', t) curve. There have been described recently many elegant methods by which this type of curve can be obtained by automatic registration, and various groups of observers are obtaining practically continuous records of this kind. It is my object in this paper, however, to emphasize the advantages of supplementing such observations by measurements made on as many frequencies as possible, and to discuss briefly two methods which have been found useful in this connexion. If we make, as nearly simultaneously as possible, a series of measurements of P' for a wide range of mean frequency f we can draw a (P', f) curve. From this it is possible to deduce the maximum electronic content of both lower and upper regions and so study the diurnal and seasonal variation of ionization. No such corresponding amount of information can be obtained from a (P', t) curve. The determination of (P', f) data with as close a frequency-spacing as possible is therefore one of the two methods advocated and discussed below. The second method is a compromise between the (P', t) and (P', f) series of measurements and will be referred to as the (P', t, f) method. With our present technique its prosecution is a less arduous matter than the rapid measurements required for hourly (P', f) curves, but it has the disadvantage that it yields information concerning the ionization in only one or other of the two reflecting regions.

§ 2. THE DETERMINATION OF (P', f) DATA

In 1930(1) it was pointed out that by measuring the critical penetration frequency for the Kennelly-Heaviside layer at different times of the day the diurnal variation of the maximum ionization content could be studied. An experimental study of the ionization of the lower region was made on these lines with (P', f) data obtained by the frequency-change method. In this case the values of f were spaced 0·25 Mc./sec. apart. On changing over to the group-retardation method at King's College in 1931, it was possible to make measurements more rapidly in time and with closer frequency-spacing and these led to the recognition of the dependence of the critical penetration frequency on the polarization of the waves. In still more recent work at the Radio Research Station, Slough, and at the Halley Stewart Laboratory, King's College, London, working in conjunction with the National Physical Laboratory, improved technique has permitted the determination of (P', f) data on frequencies 0·05 to 0·1 Mc./sec. apart, the time spent on a single frequency being about 15 sec. But even this procedure is not ideal, and it is hoped that, before long, apparatus will be developed which will yield automatically (P', f) curves comparable with the automatic records of (P', t) which are now being obtained. If, at the same time, the receiver could be made to respond either to left-handed or to right-handed circularly polarized downcoming waves the results would be still further enhanced in value.

§ 3. THE CALCULATION OF MAXIMUM IONIZATION CONTENT FROM CRITICAL FREQUENCY DETERMINATIONS

As the experiments we are considering are carried out with only a small distance between sender and receiver it is assumed that the waves are incident normally on the ionized region which reflects them, and it is assumed further that reflection takes place at a level at which the refractive index μ of the medium is reduced to zero by the presence of electrons or ions. It is recognized that the second of these assumptions is only an approximation, since it is just for the conditions in which μ is small compared with unity that the simple treatment of wireless wave propagation in terms of rays breaks down, for it is not then possible to consider the properties of the medium as remaining sensibly constant within the dimensions of a wave length in the medium. It is, however, clear from the accurate wave treatment of Hartree that, as soon as the square of the refractive index becomes slightly negative, marked reflection takes place even if the change of properties with height is not abrupt, so that, until the subject is further developed on the theoretical side, the best we can do seems to be to consider the condition $\mu^2 = 0$ as the criterion for reflection at normal incidence. Although it is most probable that further progress on the theoretical side will involve a revision of the actual magnitudes of the maximum ionization content it is unlikely that it will necessitate a marked revision of the deduced diurnal trend of this quantity.

As I have shown (2) for a magneto-optical medium such as the upper atmosphere, the condition $\mu^2 = 0$ is reached for any direction of propagation relative to the earth's magnetic field, when, approximately, either

$$N = \frac{3}{2}\frac{\pi m}{e^2} f^2 \qquad \text{......(1)},$$

or when

$$N = \frac{3}{2}\frac{\pi m}{e^2} (f^2 \pm f f_H) \qquad \text{......(2)},$$

where N is the number of electrons (of charge e and mass m) per cm^3, f is the frequency of the waves and f_H is equal to 1·32 Mc./sec., the characteristic gyro-frequency of electrons under the influence of the earth's magnetic field. If, therefore, f represents a critical frequency, N represents a maximum ionization content. Which of these formulae is applicable in any case depends on various factors. For the extraordinary ray, which is of right-handed circular polarization for the conditions we are considering, the relevant formula is (2) with the lower sign. For the ordinary ray, however, whether we use (1) or (2) with the upper sign depends on the magnitude of a certain critical ratio $2p_L\nu/p_T^2$ where p_L and p_T are the natural angular frequencies of rotation of an electron about the longitudinal and transverse components of the earth's magnetic field and ν is the frequency of electron collisions with the air molecules. If this ratio is large compared with unity the propagation resembles the longitudinal type and the appropriate formula for the ordinary wave

N, e, m, f

p_L, p_T

ν

is (2) with the upper sign. If, on the other hand, this ratio is small compared with unity the propagation resembles the transverse type and the appropriate formula is then (1). It seems fairly certain that for the upper region, where ν is small, $2p_L\nu/p_T^2$ is also small, so that we have

$$N=\frac{3}{2}\frac{\pi m}{e^2}f^2 \dots \text{(ordinary ray)} \qquad \dots\dots(3)$$

and

$$N=\frac{3}{2}\frac{\pi m}{e^2}(f^2-ff_H) \dots \text{(extraordinary ray)} \qquad \dots\dots(4).$$

It may be noted that for constant N the critical conditions may be simultaneously reached for an ordinary wave frequency of, say, f_1 and for an extraordinary wave of frequency f_2. The relation between f_1 and f_2 in this case is, evidently,

$$f_1^2=f_2^2-f_2f_H \qquad \dots\dots(5),$$

or

$$f_2-f_1=\frac{f_2}{f_2+f_1}f_H \qquad \dots\dots(6).$$

Now if f_1 and f_2 are of the order of 4 to 6 Mc./sec. as is the case in practice for the upper region, while f_H, which is determined by the magnitude of the earth's total force, is 1·32 Mc./sec., the value of (f_2-f_1), according to (6), ranges from 0·66 to 0·68 Mc./sec. We shall see later that experimental values of this order of magnitude are obtained.

For the lower ionized region where the critical conditions at noon are reached at 3 to 4 Mc./sec. according to season, the corresponding value of (f_2-f_1) ranges from 0·78 to 0·68 Mc./sec. if the conditions approximate to the transverse type of propagation. If, however, the collisional frequency is sufficiently high to make the ratio $2p_L\nu/p_T^2$ much greater than unity the propagation would approximate more closely to the longitudinal type and we should then have for the ordinary wave of frequency f_1

$$N=\frac{3}{2}\frac{\pi m}{e^2}(f_1^2+f_1f_H) \qquad \dots\dots(7)^*,$$

and, since, as before we have for the extraordinary wave

$$N=\frac{3}{2}\frac{\pi m}{e^2}(f_2^2-f_2f_H) \qquad \dots\dots(8),$$

we also have

$$f_2-f_1=f_H \qquad \dots\dots(9).$$

Summarizing, therefore, we may expect, according to conditions, values of (f_2-f_1) ranging from 0·66 to 1·32 Mc./sec.

---

* Equations (1) to (4), (7), (8) and (10) have been derived from the theory of dispersion with the inclusion of the term in the expression for the refractive index which, according to Hartree, expresses the discreteness of the scattering centres. If this term is neglected, since its inclusion is still a debatable matter, the expressions for N must all be multiplied by $\frac{2}{3}$.

§4. THE INTERPRETATION OF (P', f) DATA WITH SOME ILLUSTRATIVE EXAMPLES

At the outset it may be stated that, for the conditions we are considering, the influence of the earth's magnetic field is such that we are obliged to take into account the polarization of the returned waves, and, in fact, consider the (P', f) curves for the ordinary wave and for the extraordinary wave separately. It is found, for reflection from both regions E and F, that there are very frequently obtained echo doublets and it is rarely a matter of difficulty to decide which is the extraordinary pulse and which is the ordinary one. This interpretation follows on the lines previously discussed by Appleton and Builder(3). For conditions in which electron limitation is not operative, the ordinary ray is less absorbed, due to collisional friction, than is the extraordinary ray. This may be predicted from theory for the range of frequencies we are considering and is found to be the case in practice. If, moreover, the records of echo-delineation are made with a time base which is locked to the electrical mains which control the pulse-frequency of the sender, it is possible to photograph the echo patterns for the different frequencies successively on the same record, so that the ground reference pulses are immediately under one another in a straight line. From such a record the tracing of the separate (P', f) curves for the ordinary and extraordinary rays is a simple matter. When the successive photographs have been obtained with small frequency spacing one can, on looking along the record, see immediately the different run of the two curves*.

For the upper region the importance of magneto-ionic double refraction is now well established. Until recently there was some doubt concerning its influence in causing echo-doubling in reflection from the lower region, although it was known that characteristic polarizations due to differential absorption were thereby produced. This doubt has been recently removed by experiments carried out in this laboratory by Mr F. W. G. White, who has shown that magneto-ionic splitting is present for region-E reflection as in the case of region-F reflection, but that, owing to marked absorption, the extraordinary ray is usually very weak in intensity. In some of the data discussed below examples of E-region splitting can be clearly recognized, confirming the results of Mr White†.

Before we proceed to discuss typical (P', f) curves it may be well to consider the type of curve to be expected if there are in the ionosphere, at any time, two main regions of electrification, the upper region being more strongly ionized than the lower. For the lower frequencies we should expect the reflection of both components from the lower region, the extraordinary ray being strongly absorbed. With increasing frequency the ordinary ray will be the first to suffer electron limitation and so, penetrating region *E*, will be reflected at region *F*. With increasing frequency the extraordinary ray will also eventually penetrate region *E* and then both rays will be reflected from the upper region. The two types of magneto-ionic splitting described by Appleton and Builder as "group-retardation splitting" and "stratification splitting" may then be expected to occur in the order named, until with still higher frequencies the penetration of the upper region by the ordinary and extraordinary rays takes place in succession. The examples taken for discussion below are all found to be broadly explicable on such lines but in some cases illustrate also phenomena not previously described.

---

* For a description of the apparatus used see *The Cathode-ray Oscillograph in Radio Research*, by Watt, Herd and Bainbridge-Bell (London, 1933).

† As has previously been pointed out(4), the difference between the absorption of the extraordinary and ordinary waves is most marked for the critical gyro-frequency 1·32 Mc./sec., so that for frequencies about this value only the ordinary ray reaches the ground in appreciable intensity. The results of Meissner(5), who found no anomalies for a wave length of 212 metres, are thus explained

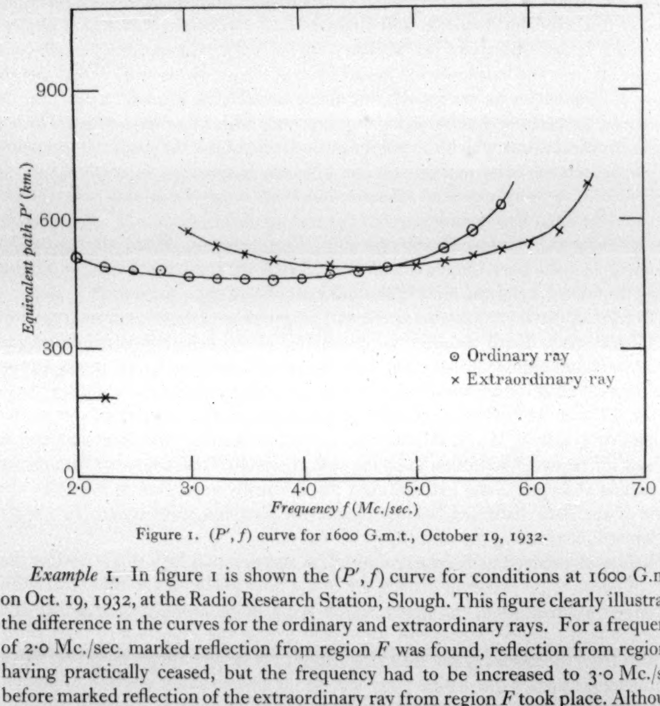


Figure 1. (P', f) curve for 1600 G.m.t., October 19, 1932.

Example 1. In figure 1 is shown the (P', f) curve for conditions at 1600 G.m.t. on Oct. 19, 1932, at the Radio Research Station, Slough. This figure clearly illustrates the difference in the curves for the ordinary and extraordinary rays. For a frequency of 2·0 Mc./sec. marked reflection from region *F* was found, reflection from region *E* having practically ceased, but the frequency had to be increased to 3·0 Mc./sec. before marked reflection of the extraordinary ray from region *F* took place. Although low echo-amplitude, due no doubt to absorption, prevented an accurate determination of the critical frequencies f_1 and f_2 for region *F*, the general trend of the curves shows that the quantity $(f_2 - f_1)$ was about 0·66 Mc./sec., in agreement with equation (6) above for the quasi-transverse type of propagation. It will be seen that both group-retardation splitting and stratification splitting are well illustrated in figure 1.

Example 2. In figure 2 is shown the (P', f) curve for conditions at noon on April 10, 1933, at the Radio Research Station, Slough. Here the region-E splitting is clearly shown. At about 3·0 Mc./sec. the change-over from reflection at region E to reflection at region F took place. At first the increase of equivalent path with increase of frequency for reflection at region F was not marked. With a further increase of frequency, however, greater penetration of the upper region took place and P' reached a maximum at 4·2 Mc./sec. (The significance of this maximum is further discussed below.) The fall in P' with further increase of frequency suggests another group-retardation effect. Ultimately the ordinary ray penetrated region F at 5·6 Mc./sec.

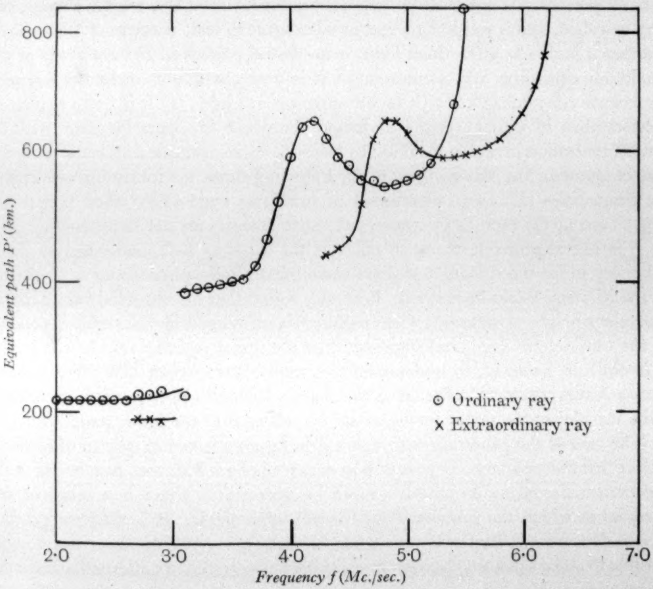


Figure 2. (P', f) curve for 1200 G.m.t., April 10, 1933.

It will be seen that the curve for the extraordinary ray has quite a similar trend but is displaced 0·70 Mc./sec. on the frequency scale. This difference is approximately that mentioned above for the difference $(f_2 - f_1)$ between the critical penetration frequencies for quasi-transverse propagation. That the same frequency-spacing is maintained for frequencies lower than these penetration values is no doubt due to the fact that, in the range of frequencies we are considering, the transmission characteristics of an ordinary ray of any frequency f_0 Mc./sec. are not markedly different from those of an extraordinary ray of frequency $(f_0 + 0{\cdot}66)$ Mc./sec. To calculate

$N_{\max.}$ for region F from the critical penetration frequency for the ordinary wave equation (3) is the appropriate formula, while in the case of the extraordinary wave equation (4) should be used. It is clear from the critical frequency-spacing that the values obtained in either case would be approximately the same.

The maximum in the (P', f) curve for region F is a phenomenon not previously recorded and clearly indicates a variation in ionization with height different from that calculated on the assumption of a single monochromatic ionizing radiation acting on the earth's atmosphere. The fact that for frequencies higher than 4·3 Mc./sec. the equivalent height falls with increasing frequency indicates that there must be a sudden increase of ionization with height at a particular value of ionization. At present it is not quite certain what is the cause of this region-F ledge, as it may be called, and it would be a matter of interest to test, at the next solar eclipse, whether it is due to ultra-violet light or to neutral particles. From a study of this maximum extending over some months it is now possible to make the following statements concerning it: (*a*) it is not apparent at night; (*b*) it is more marked in summer than in winter; (*c*) the frequency for which it occurs increases with the general ionization in region F caused by the sun. As an example of this the following may be quoted. On May 9, 1933, at the following times the maximum occurred at the frequencies (Mc./sec.) mentioned in brackets: 0700 (3·8); 0800 (4·0); 1000 (4·3); 1200 (4·5); 1400 (4·3); 1600 (4·1); 1900 (maximum not detectable).

It is not improbable that this effect is the same as that mentioned by T. L. Eckersley in his discussion$^{(6)}$ of short-wave transmission phenomena as elucidated by the Marconi facsimile method. Eckersley found that his observed values for the equivalent height of reflection from region F were ranged in two series depending on the wave length used, and suggested that the upper region might be composite. It is difficult, however, to understand this author's statement that the lower-frequency waves would be reflected at the sharply defined upper portion of region F while the higher-frequency waves would be reflected at the lower part.

The case of the penetration of region E in figure 2 is not so easy to unravel. It is clear that the ordinary-ray penetration occurred at 3·0 Mc./sec., but, owing to the low extraordinary-ray amplitude caused by absorption, there is a range of frequencies in which the echo-amplitude is not appreciable. It is thus not possible here to determine f_2 for the lower region, so that, $(f_2 - f_1)$ being uncertain, it is not possible to make a definite decision in choosing between the two alternative formulae for calculating $N_{\max.}$.

Example 3. In figure 3 is shown the (P', f) curve obtained at noon on April 8, 1933, at the Radio Research Station, Slough. This curve is of special interest as showing reflection from equivalent heights between region E and region F. Many measurements made within the last few years have forced on us the necessity of recognizing that reflection can, on occasion, take place at such an *intermediate region*, as it may be called. Such a region is detected rarely at noon, but more frequently in the early morning.

In this figure is clearly seen the effect of splitting in region E. The fall in P' with increase of frequency for the intermediate region indicates that there is a discontinuous jump here in the case of the ordinary-ray curve. It is clear that the intermediate region is not the same as the region-F ledge, for the maximum indicating the influence of the latter is found at a much higher frequency.

Example 4. The (P', f) data exhibited in figures 4 and 5 may be conveniently considered together, since they were obtained on the same day, May 9, 1933, at the Radio Research Station, Slough. Figure 4 represents conditions at 0800 G.m.t. and is of interest as showing very clearly the splitting in region E*. Moreover, the magnitude of the frequency separation between the ordinary and extraordinary curves here strongly suggests quasi-transverse conditions. In figure 4 the shelf maximum in region F is not very marked since it is an early morning curve.

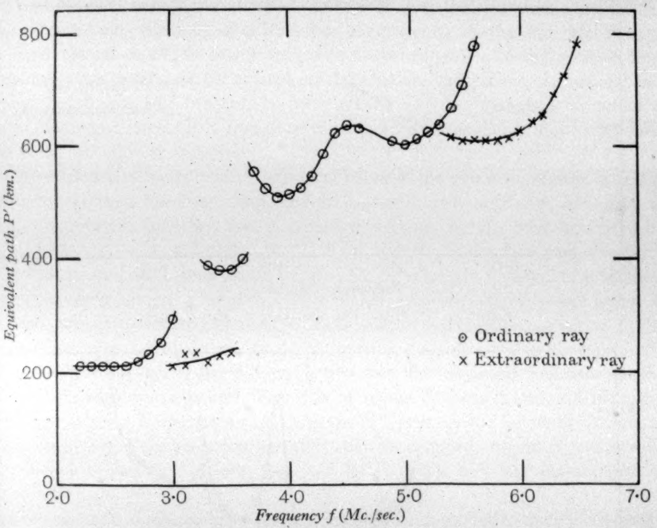


Figure 3. (P', f) curve at 1200 G.m.t., April 8, 1933.

In figure 5, which represents conditions on the same day at 1000 G.m.t., we note that again splitting is marked in region E. Also the ordinary-ray curve is seen to include values for P' almost up to region-F values. Although part of these abnormally high equivalent heights may be regarded as due to group-retardation effects (we may compare in this connexion the high values for P' for frequencies

---

[*] A word of caution is needed here, since double echoes from region E are often noted which do not consist of magneto-ionic components. Sometimes we have simultaneous reflection from regions EI and EII, while sometimes we have simultaneous reflection from region E caused by ultra-violet light and from the ionized region produced, at a slightly lower height, by abnormal ionizing agencies, e.g. corpuscles. Such abnormal ionization has been shown by Mr Naismith and the writer, *Proc. R. S.* A, **137**, 36 (1932), and *Proc. Phys. Soc.* **45**, 389 (1933), to be correlated either with magnetic storms or with thunderstorms.

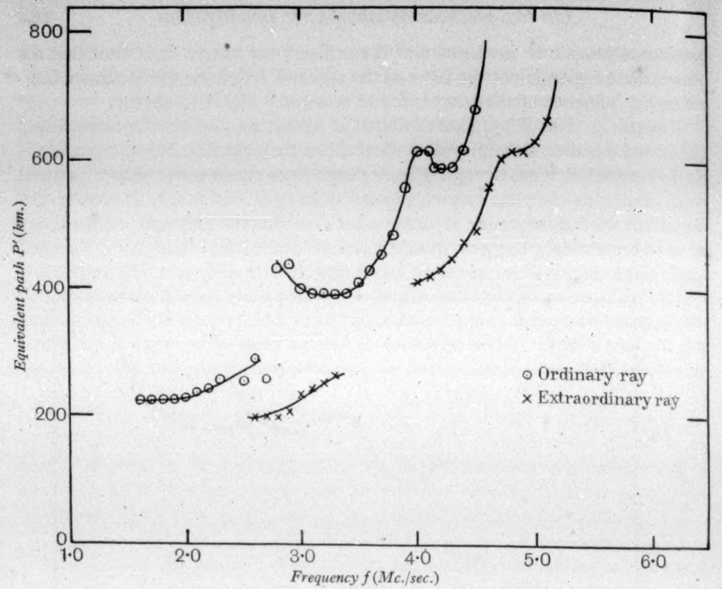


Figure 4. (P', f) curve at 0800 G.m.t., May 9, 1933.

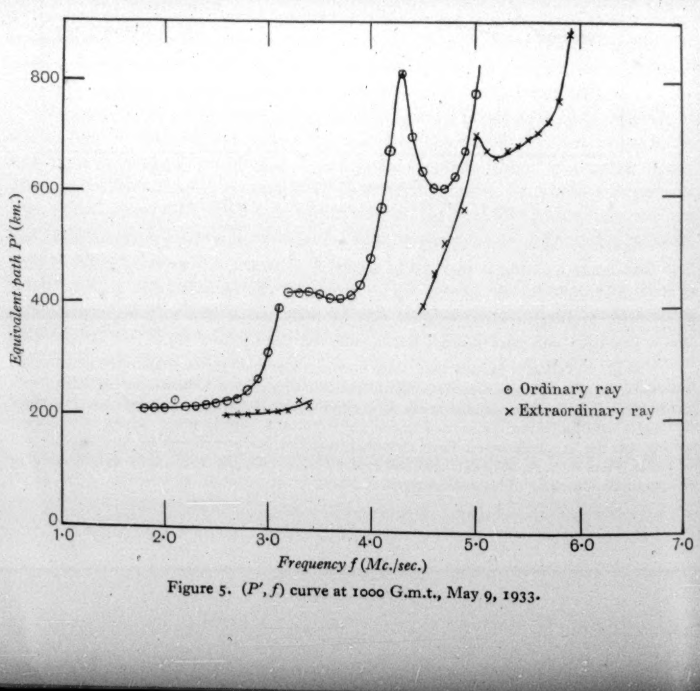


Figure 5. (P', f) curve at 1000 G.m.t., May 9, 1933.

approaching the region-F penetration values), it is unlikely that the whole effect is due to this cause and we must conclude that there is a considerable amount of ionization between the two main regions. Further reference will be made to this point in the discussion below.

For the region-F parts of the curves the shelf-maximum has become more pronounced as noon is more nearly approached. Moreover, at 1000 G.m.t. it now occurs for the ordinary ray at 4·3 Mc./sec. whereas two hours earlier (see figure 4) it occurred at 4·05 Mc./sec.

§ 5. FURTHER DISCUSSION OF THE ILLUSTRATIVE EXAMPLES

From the data briefly summarized above it is clear that we must consider the ionosphere as being made up of at least four components. As the data refer to days free from anomalous effects due to magnetic disturbances it is clear that these four components are produced by normal solar radiation. Moreover, the general dependence of the electron contents on solar altitude also indicates that the radiation travels in straight lines. It is therefore considered most probable that ultra-violet light is the radiation in question.

The existence of considerable ionization between the two main regions E and F during the daytime has been suspected for a considerable time now, but since, at noon, it is normally less than that in region E it cannot usually be investigated by the methods we are considering. In the early morning hours, however, the sun's rays ionize successively lower strata which have been largely depleted of ionization during the night, so that the intermediate region becomes ionized before region E has been sufficiently ionized to mask it. Reflection in succession from region F, the intermediate region, and region E is therefore frequently observed in the morning*. On the exceptional day of April 8, 1933, however, the maximum ionization in the intermediate region was greater than that of region E about noon, and from the critical penetration frequencies read from the (P', f) curve the following maximum ionization-densities (in electrons per cm.^{3}) may be deduced: region E $(1·8 \times 10^5)$; intermediate region $(2·5 \times 10^5)$; region-F ledge $(3·8 \times 10^5)$ and main region F $(6·1 \times 10^5)$.

The existence of the region-F ledge is inferred from the fall in equivalent height with increase of frequency—see, for example, figure 2. The frequency at which the maximum occurs on the region-F portion of the (P', f) curve may be taken as being approximately the penetration frequency of the ledge. Waves of frequency immediately higher than this value do not reach much greater heights, and the reduction of P' with increase of f is due to the reduction in the group-retardation effect of the ledge itself. For the conditions indicated by figure 2 the electron-distribution with height must be somewhat as shown in figure 6, where the relative values of the ordinates are approximately correct but not those of the abscissae.

Concerning the question of nomenclature, since it is still clearly necessary to retain the division into the two main reflecting regions E and F, it is suggested that the four components should be designated as shown in this diagram. In this connexion it is convenient to retain capital-letter symbols to designate regions caused by normal solar influence and to use small-letter symbols for regions caused by abnormal agencies.

---

* J. A. Ratcliffe and E. L. C. White have obtained independent evidence of this using their method of automatic registration of layer heights.

Such a composite structure as I have pictured for the ionosphere is not considered unlikely when it is remembered that Pannekoek(7) has shown that the level of the maximum ionization caused by ultra-violet light depends on the ionization potential of the gaseous constituent in question. We might therefore expect a maximum of ionization for each constituent, atomic or molecular. As, however, there is laboratory evidence that ionization can be produced by photons of energy less than that corresponding to the ionization potential, it is probable that the matter is further complicated by the processes of cumulative ionization.

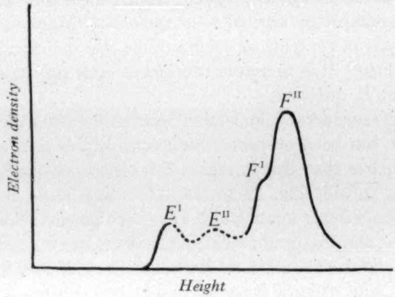


Figure 6.

§6. THE DETERMINATION AND INTERPRETATION OF (P', t, f) DATA

As has previously been mentioned the (P', t, f) method is a compromise between the methods involving the determination of (P', t) and (P', f) data. It requires a certain amount of prevision on the part of the observer in that he has to anticipate whether the ionization is increasing or decreasing. For the case of the normal ionization produced by the ultra-violet light from the sun there are now sufficient data to guide one in this respect, but the weakness of the method is that it is difficult to prosecute during conditions of abnormal ionization.

Let us consider a simple normal case as an illustration. During the night, from about midnight till about an hour before sunrise, it is usual for the ionization in the upper region to decrease steadily. Let us suppose that at the beginning of this period we work with a frequency which is just less than the critical penetration value for the extraordinary wave. (For such conditions the ordinary wave will be penetrating the region in question.) If a (P', t) curve is obtained, by automatic registration or otherwise, the usual gradual increase of P' with t will be noticed and recorded and eventually there will be no appreciable reflection. The frequency can then be changed to a slightly lower value (0·2 Mc./sec. steps are convenient) and the process repeated. In the case of increasing ionization, as in the early morning period, the corresponding steps are, of course, increases in frequency. From the examination of the record we obtain in this way the times at which extraordinary waves of different frequencies penetrate the region.

An example of the type of record obtained in this way is shown in figure 7, where the equivalent height was automatically registered during the three hours 0000 to 0300 G.m.t. on April 26, 1933, in an experiment carried out at the Radio Research Station, Slough. The going out of the extraordinary wave for the five frequencies 4·0, 3·8, 3·6, 3·4 and 3·3 Mc./sec. in order is seen to occur at the following times: 0009, 0051, 0126, 0215 and 0248 G.m.t.

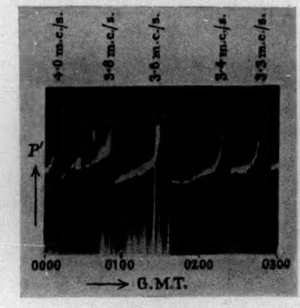


Figure 7. Relation between equivalent path P' and time on April 26, 1933.

To calculate the maximum electronic content at these times we insert the appropriate frequencies in the formula

$$N = \frac{3}{2}\frac{\pi m}{e^2}(f^2 - ff_H) = 1{\cdot}86 \times 10^{-8}(f^2 - ff_H) \qquad \ldots\ldots(10),$$

where f_H is 1·32 Mc./sec.

We are thus able to plot a curve illustrating the variation of $N_{\text{max.}}$ with time. In figure 8 are shown the results of the run of which figure 7 is an illustrative record. Here the ionization is seen to be decreasing rapidly at first, but, at 2230, the rate of decrease is much reduced and continues to remain so throughout the greater part of the night. This reduction in the rate of the disappearance of the ionization is not understood, unless it be due to the fact that the height at which the maximum ionization exists increases with time (as, indeed, the records show that it does), so that the pressure and thus the magnitude of the recombination or attachment processes decrease correspondingly. The ionization is seen to begin to increase at least 45 minutes before ground sunrise, a phenomenon which is to be expected in a region at a considerable height above the earth's surface.

It is not proposed to consider here the full significance of the information depicted in figure 8, as obviously at least a full year's data of this type would be required for adequate discussion. One or two points, however, may be mentioned. In examining the decay of ionization during the period 2230 to 0315, for which period the curve suggests steady conditions, we are naturally led to enquire how far the dissipative process conforms with the usually accepted law of recombination which is expressed by the formula

$$\frac{1}{N}-\frac{1}{N_0}=\alpha t \qquad \text{......(11)},$$

N_0, N where N_0 is the electron-concentration at zero time and N the concentration at any
t subsequent time t. On plotting $(N^{-1}-N_0^{-1})$ against t, however, we obtain a curve

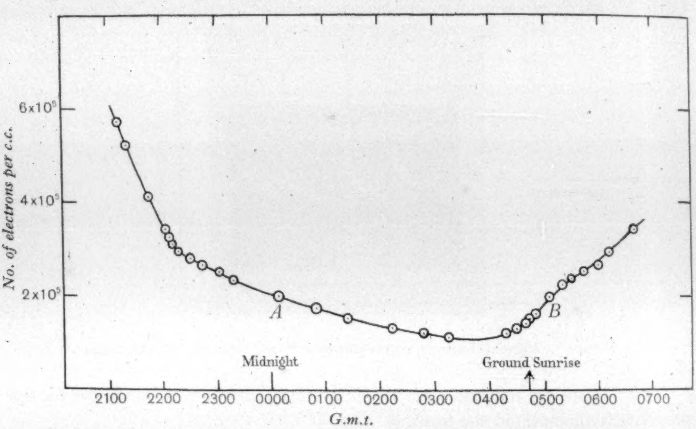


Figure 8. Curve showing variation of ionization in upper region, April 25–26, 1933.

which is not straight but definitely concave upwards, indicating an increase of α with time. This would indicate, contrary to the conclusions of Eckersley(8), that equation (11) is not strictly valid during this period. If, however, we choose to represent approximately the sequence of events in terms of recombination according to equation (11) we may remark that the numerical value of α ranges from $2{\cdot}5 \times 10^{-10}$ to $4{\cdot}0 \times 10^{-10}$.

There is, however, another process which may gradually render the electrons ineffective during the night, namely, their attachment to neutral atoms. In this case we should expect the following relation to hold in place of equation (11):

$$\log N_0 - \log N = \beta t \qquad \text{......(12)},$$

β where β is the attachment coefficient. Here a plot of $\log N$ with t gives a curve which is fairly straight and a numerical value for β of $6{\cdot}0 \times 10^{-5}$. The matter cannot, however, be regarded as settled and is reserved for a later discussion.

From a curve such as that shown in figure 8 data concerning the rate of production of ionization may be deduced. Consider a point on the falling part of the curve, for instance A. Then the slope of the curve $(dN/dt)_A$ represents the rate at which the electrons are disappearing. Now at a corresponding point B on the rising part of the curve where the ionization is the same, the rate of increase of ionization $(dN/dt)_B$ is determined by two factors, (i) the electron dissipative process, and (ii) the rate of production q of electrons. Since we may assume that for similar magnitudes of ionization the rate of disappearance of electrons is the same we see that q is equal to the numerical sum of $(dN/dt)_A$ and $(dN/dt)_B$.

Making use of such theoretical considerations for the data illustrated in figure 8 we find that the rate of electron-production increases with time as shown in the table.

G.m.t. April 26, 1933	0345	0421	0446	0530	0616
q (electrons per cm^3 per sec.)	0	21	30	38	55

§7. ACKNOWLEDGMENTS

The work described in this paper was carried out as part of the programme of the Radio Research Board of the Department of Scientific and Industrial Research. I am indebted to Mr R. A. Watson Watt and Mr J. F. Herd for providing facilities for its prosecution at the Radio Research Station, Slough, and also to them and to my collaborator, Mr R. Naismith, for much helpful discussion. I also wish to thank Mr G. H. Calver for much valued assistance in making the measurements.

Note added June 6. When this paper was ready for publication a most interesting letter by Messrs Schafer and Goodall appeared in the issue of *Nature* for June 3, 1933, in which very similar results concerning the structure of the ionosphere are announced as a result of their observations in America. The opportunity of comparing the full account of their methods and data with that given in the present paper is awaited with much interest.

REFERENCES

(1) E. V. Appleton. *Nature*, Feb. 7, 1931; see also E. V. Appleton and R. Naismith, *Proc. R. S.* A, **137**, 36 (1932).
(2) E. V. Appleton. *Proc. Inter. Sci. Rad. Union*, **1** (Washington, 1927).
(3) E. V. Appleton and G. Builder. *Proc. Phys. Soc.* **44**, 76 (1932).
(4) E. V. Appleton. *Electrician*, **907**, 257 (1927); and *Proc. Inter. Sci. Rad. Union*, **1** (Washington, 1927).
(5) A. Meissner. *Elek. Nach. Tech.* **3**, 321 (1926).
(6) T. L. Eckersley. *J. Inst. E. E.* **71**, 423 (1932).
(7) A. Pannekoek. *Amst. Acad. Proc.* **29**, 1165 (1926).
(8) T. L. Eckersley. *Loc. cit.* p. 420.

DISCUSSION

Mr A. O. Rankine. I would like to ask Prof. Appleton to explain the use of the terms "ordinary" and "extraordinary" in relation to the rays discovered in his remarkable experiments. He has spoken of the two reflected beams as being circularly polarized in opposite senses, a phenomenon which in optics is associated with rotation of the plane of polarization in optically active substances or in other transparent materials stimulated by a magnetic field. These two rays, discovered and explained by Fresnel, are not usually called "ordinary" and "extraordinary," although in the special case of quartz, which displays optical activity along its axis as well as birefringence in other directions, it is clear that the two effects are closely interlinked. Is the effect of the earth's magnetic field on the ionosphere simply that of imparted optical activity—the Faraday effect—or does it produce double refraction in the generally accepted sense as well?

Author's reply. The influence of the earth's magnetic field on the ionosphere is similar to that with which we are familiar in the case of the Faraday effect where, as Prof. Rankine expresses it, optical activity is imparted to the medium by the imposed magnetic field. Rotation of the plane of polarization occurs for propagation along the direction of the magnetic field and double refraction for propagation at right angles. Of the two component waves, one is little influenced by the action of the field while the other is much influenced and exhibits anomalous-dispersion phenomena at the natural gyro-frequency. These two components have (most probably without justification, I fear) been respectively termed the "ordinary wave" and the "extraordinary wave."

535·33:537·531

STUDIES IN THE EXTREME ULTRAVIOLET AND THE VERY SOFT X-RAY REGION

The Eighteenth Guthrie Lecture, delivered on June 16, 1933,

BY PROF. M. SIEGBAHN

§ 1. INTRODUCTION

ONLY a few years ago X-ray spectra and optical spectra were separated by a rather large gap, extending over 3 or 4 octaves of wave-lengths. The spectroscopic methods used at that time for studying these two ranges were qualitatively different. In the X-ray region, crystal lattices were the only effective means for the analysis of the radiation. The fundamental formula

$$n\lambda = 2d . \sin \phi$$

shows that the method is limited to values of λ which are smaller than $2d$, where d is the distance between the atomic layers serving as reflecting planes. In practice this means that the crystal lattice method is limited to wave-lengths below, say, 20 Å.

On the other hand it had been shown by Millikan that the ruled grating used in the manner adopted at that time could register optical spectra of wave-lengths down to, say, 200 or 300 Å.; in a few cases some shorter wave-lengths had been observed.

A new era of the spectroscopy was begun when advantage was taken of the experimental fact that radiation of short wave-length was strongly reflected at grazing incidence. By using plane and concave ruled gratings it was thus possible at least in principle to cover all the formerly unknown region between the X-ray and extreme ultraviolet regions. Experimentally there were many problems to be solved before the expected results could be gained. It will be the object of this lecture to give a preliminary report on some of the work done on these problems at the laboratory of Upsala during the past year.

§ 2. THE USE OF RULED GRATINGS IN THE EXTREME ULTRAVIOLET AND THE VERY SOFT X-RAY REGION

Figure 1 illustrates the effects obtained with concave and plane gratings. In the earlier experiments for registering the short-wave-length region the radiation was reflected at incidence nearly normal to the concave grating as at (I). In the new methods (II, III) the incoming radiation strikes the grating at an angle of only a few degrees. From the geometry of the concave grating it is immediately seen that this also means that the plate, which must be bent to the Rowland circle, receives the radiation at a very small angle as at (II). This gives rise to an experimental difficulty which increases greatly as soon as one tries to diminish further the angle of incidence, as is necessary for registering the shortest wave-lengths.

In this respect the plane grating (III) has the advantage that the plate is placed nearly normally to the radiation. But to get well-defined lines in this case it is necessary to cut out a small pencil of radiation by means either of two narrow slits or of one slit used with a very small grating. Both these methods have been used. Up to this time practically all results in the very soft X-ray region have been achieved by the plane-grating method.

In comparison with the concave grating, the plane grating has decided disadvantages which make it desirable to try to apply the former to this region also. It is to be remembered that the pencils of rays at the plane grating are always divergent, so that sharpness of the lines can only be obtained by diminishing the width of the pencil and thereby reducing the number of lines of the grating which are effective. As the resolving-power is determined by this number, the plane-grating method is far inferior to the concave-grating, giving only $\frac{1}{10}$ to $\frac{1}{100}$ of the resolution obtainable with the latter. For these reasons our efforts have been devoted to further development of the concave-grating method with the object of using it for the very soft X-ray region.

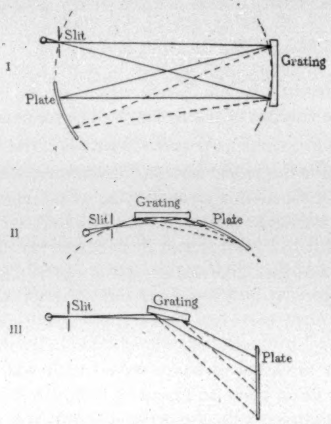


Figure 1.

§ 3. CONCAVE GRATINGS FOR THE VERY SOFT X-RAY REGION

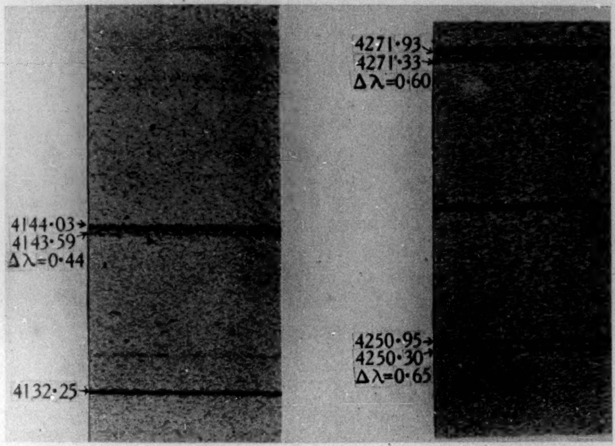
The concave-grating method has been used at the Upsala laboratory during the last 5 years for extensive investigations of the optical spectra in the extreme ultraviolet*. In this case the light-source has been a spark gap in a high vacuum directly connected to the spectrometer and separated from this only by the slit. In some cases it was possible in these experiments to register *optical* spectrum lines with wave-lengths as small as 40 Å.

---

* By Edlén, Ericsson, Ekefors, Arvidsson, Mack, Söderqvist, Borg and others.

In spite of this, the researches carried out upon very soft X-rays in this region with the same spectroscopic outfit were not successful. During the past year, however, it has yet been possible to find the right experimental conditions for obtaining well-defined lines from X-ray spectra.

One of the main problems in the further development of the concave-grating method with very small angles of grazing incidence was the production of suitable gratings. In particular, it was to be expected that an improvement of the ruling on glass would secure better results, as had been the case in our earlier experiments* with small plane gratings. For this purpose a ruling-engine was constructed and built in the workshop of the laboratory during the past year. Special care was devoted to the ruling-mechanism and the technique of ruling. The gratings which have been ruled on the new machine show an absolutely smooth surface, the lines having the same appearance at the beginning as at the end. The big groove usually found at the beginning of the lines has been entirely eliminated. Gratings up to about 10 cm. may be ruled on the new engine, but the optimum width of the concave gratings used at grazing incidence is considerably less than this, namely 20 to 40 mm.



a *b*

Figure 2.

A test of some of the gratings with ordinary optical light showed that the theoretical resolution was attained. Figures 2 *a* and *b* are reproductions of two spectrograms of narrow doublets from the mercury arc. The grating has about 10,000 lines (576 lines per millimetre) and its radius is about 1·8 m. The ruled surface is about 20 mm. wide, which is the optimum width for a grating used with an angle of 3° to 5° for the incident radiation.

---

* Siegbahn and Magnusson: *Z. f. Phys.* **62**, 435 (1930).

Further tests of the gratings were carried out with extreme ultraviolet radiation from optical spectra where the region below 100 Å. was of especial interest. The spark spectra from Al and Cu are reproduced in the figures 3 and 4. The original spectrograms show sharp and well-defined lines down to and below 50 Å.

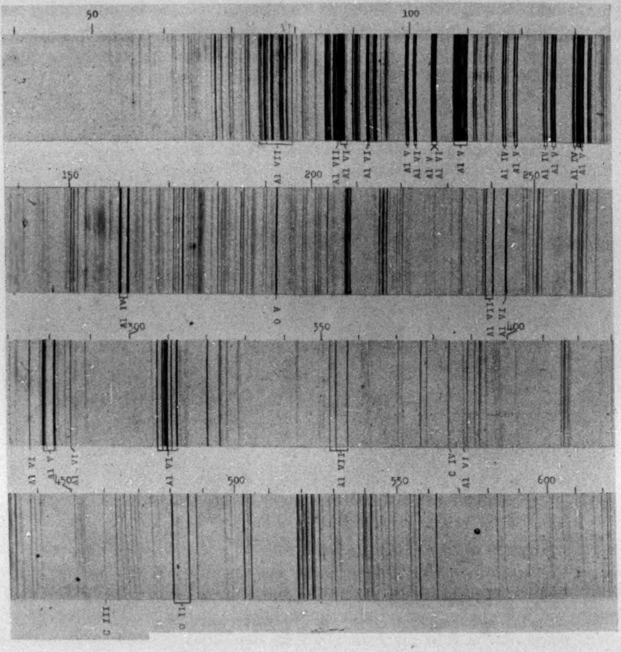

50
100
Al VII
Al VII
Al VI
Al VI
Al V
Al VI
Al V
Al VI
Al V
Al IV
Al V
Al IV
Al V
Al IV
Al V
150
200
250
Al VI
O V
Al VII
Al VI
300
350
400
Al VI
Al V
Al VI
Al VI
Al VII
C IV
Al VI
450
500
550
600
C III
O III

Figure 3. Vacuum spark spectrum of aluminium. 750 sparks, 60 kV., 0·5 μF. Glass-grating T.K. 111, 288 lines/mm., radius 1·8 m., $\phi = 3° 56'$, slit 4μ. Magnification 2·2. Upsala, May 1933.

The enlargements, figure 5, of the Al-groups at 104 Å. in the 4th order are of special interest, as corresponding photographs taken with other gratings have formerly been published*. In spite of the fact that here a grating with only 288 lines per millimetre was used, the resolution is better than formerly and especially the diffuse blackening in the neighbourhood of the lines is reduced so that faint lines near to the strong ones become visible.

---

* Ekefors: *Phys. Z.* **31**, 737 (1930). Söderqvist und Edlén: *Z. f. Phys.* **69**, 359 (1931).

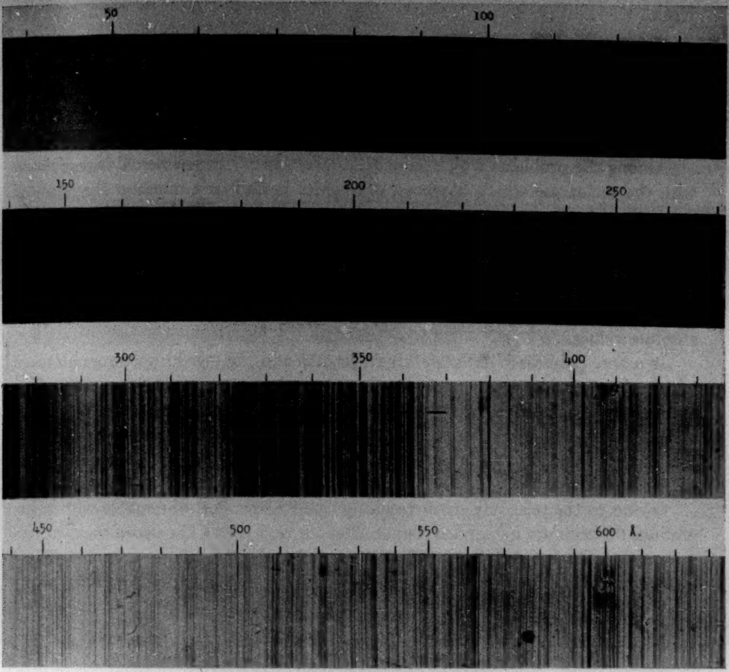


Figure 4. Vacuum spark spectrum of Cu. 750 sparks, 60 kV., 0·5 μF. Glass-grating T.K. 111, 288 lines/mm., radius 1·8 m., $\phi=3° 56'$, slit 4μ. Magnification 2·5. Upsala, April 1933.

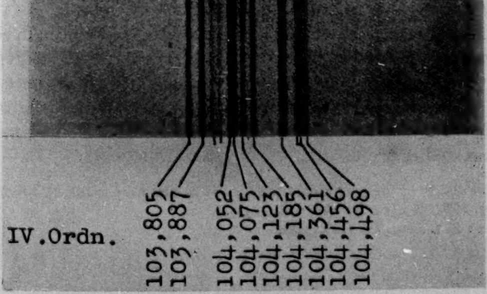


Figure 5 Al groups at 104 Å. in the 4th order. Magnification 25. Grating T.K. 111.

§ 4. ABSOLUTE MEASUREMENT OF X-RAY WAVE-LENGTHS

Among the problems which have been taken up for experimental investigation with the technique which has been developed I shall first mention the absolute determination of the X-ray wave-lengths, that is to say their values referred to the metric standard. This is of considerable interest as the X-ray measurements carried out with crystals have given us the ratio of these wave-lengths to the dimensions of the crystal lattices, so that a knowledge of the wave-lengths in absolute values will also make possible a direct computation of the atomic distances in absolute values.

In a note published in *Nature* Mr Söderman and I showed a spectrogram taken with a plane grating in which two spectra, one from an X-ray source and the other from a spark, were taken side by side with identical arrangement of the slit, grating and plate. As the optical spectrum contained a number of spectral lines whose wave-lengths were known in absolute values, the X-ray lines could be determined on the same scale.

Owing to the relatively small resolution and dispersion obtainable with plane gratings the accuracy in this determination is not very large. The use of the concave-grating technique now at hand will allow of a considerably higher accuracy. These investigations are now in progress and will soon be published by Mr Söderman.

§ 5. THE STRUCTURE OF THE X-RAY LINES AND THEIR DEPENDENCE ON THE CHEMICAL AND PHYSICAL STATE OF THE EMITTING ATOMS

The higher resolution and dispersion given by the concave grating makes it possible to resolve and study the structure of lines which with the plane grating appear to be single. In the case of the carbon K_α line, which has been studied by several investigators, the plate reproduced in figure 6 and showing side by side a spark spectrum (aluminium) with known lines and the carbon K_α line permit of an accurate determination of the wave-length. At the same time the spectrogram shows that this line has an extended structure* with at least two maxima. From figure 7 it is seen that the accuracy with which the wave-length can be determined is limited by the broad structure of the line itself; the precision of the scale of wave-lengths given by the sharp optical lines is too great to be fully utilized.

Further, it may be mentioned that the structure and wave-length are dependent on the chemical state; this has been shown by Glocker and Renninger† and was confirmed in these investigations. It is to be expected that such effects will be more pronounced in the still softer X-ray region accessible to the present methods. For the knowledge of the energy-levels in the solid state valuable information is to be expected from studies of this kind.

---

[*] During the course of these investigations similar results were found by Morand and Hautot: *Comptes Rendus*, **195**, 1383 (1932); **196**, 688 (1933).

[†] Renninger: *Z. f. Phys.* **78**, 510 (1932).

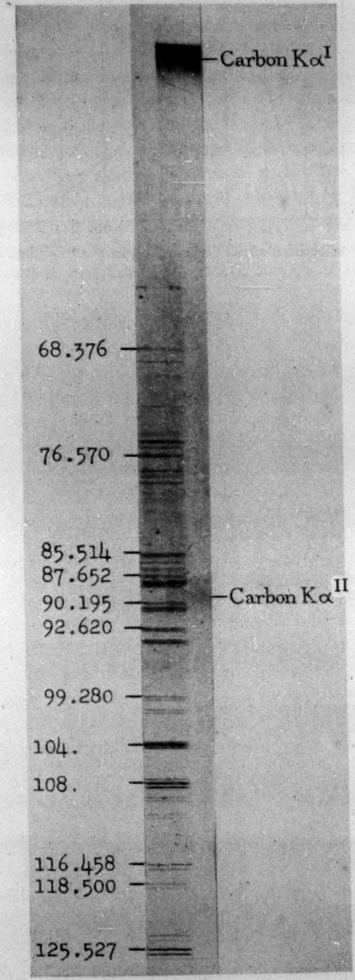

Carbon Kα^I
68.376
76.570
85.514
87.652
90.195
92.620
Carbon Kα^II
99.280
104.
108.
116.458
118.500
125.527

Figure 6.

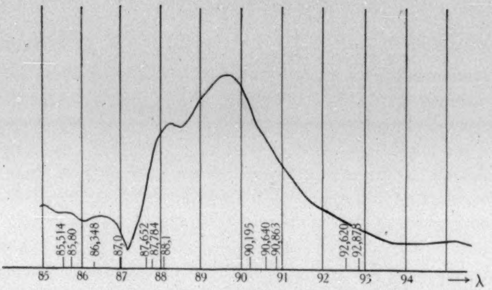


Figure 7. Photometrical registration of the Carbon $K\alpha_{II}$ line on the plate reproduced in figure 6.

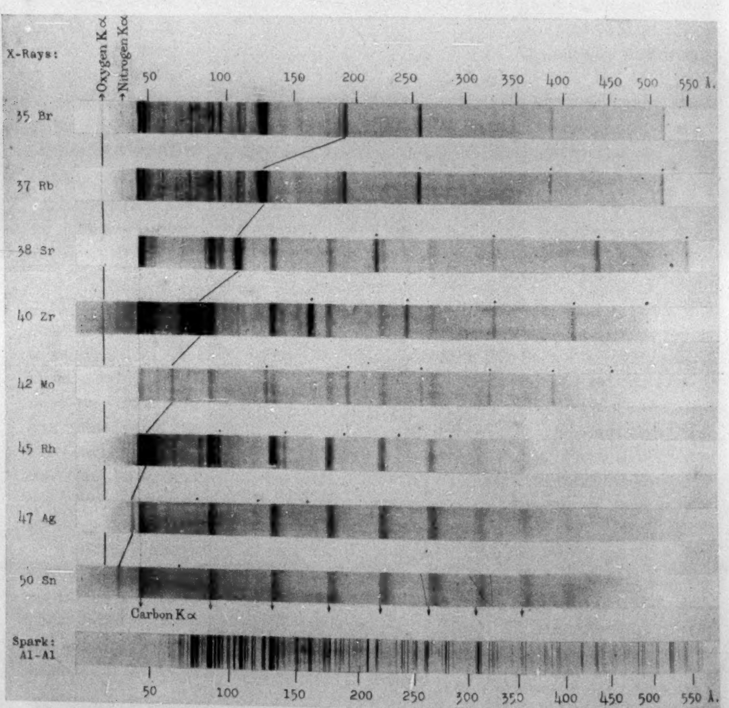

X-Rays:
→Oxygen Kα
→Nitrogen Kα
50
100
150
200
250
300
350
400
450
500
550 Å.
35 Br
37 Rb
38 Sr
40 Zr
42 Mo
45 Rh
47 Ag
50 Sn
Carbon Kα
Spark:
Al-Al

Figure 8. X-ray spectra from the elements 35 Br to 50 Sn in the very soft X-ray region 20–250 Å., and the optical spark spectrum of Al for comparison. Most of the plates show the Carbon K_α line in many orders.

§ 6. AN EXTENSION OF THE X-RAY SERIES

Of the three well-known X-ray series, the K series has been followed down to 4 (Be) at the wave-length 115 determined by Söderman in 1929 with the plane grating. The L series by the same method has been found down to 20 (Ca) at about 41 Å. by Kellström (1929). The M series in the same way was extended to 39 (Y) with one line at 93 Å. by Prins and Taken. Finally it may be mentioned that for the heaviest elements a few lines in this region (40 to 100 Å.) have been found which must be assigned to the N series or possibly to an O series.

During recent weeks some spectrograms of the elements 50 (Sn) to 34 (Se) were taken for a preliminary investigation. A set of these spectrograms is given in figure 8. In most of them the carbon K line (45 Å.) is to be seen in many orders; further, the oxygen line at 23·6 Å. and the nitrogen line at 31·6 Å. are more or less visible on all spectrograms.

A great number of hitherto unknown lines is to be found on the plates. The strongest line is due to the transition M_V–N_{III} (or M_{IV}–N_{II}) which for the four lowest elements 38 (Sr), 37 (Rb), 35 (Br) and 34 (Se) has the wave-lengths 109, 128, 193, and 230 Å., respectively, according to provisional measurements. For the lower elements the line is split up into two or more components. This same line has been measured, with a crystal-lattice for elements from 92 (U) to 63 (Eu) by Hjalmar (1923) and Lindberg (1931), and with a plane grating for the elements 51 (Sb) to 39 (Y) by Prins and Taken (1932).

§ 7. ABSORPTION SPECTRA IN THE VERY SOFT X-RAY REGION

The absorption spectra in the very soft X-ray region have only been studied in a very few cases. Thibaud (1928) registered by the plane-grating method the K absorption discontinuities for 8 (O), 7 (N) and 6 (C) at 23·5, 31·1 and 43·5 Å. respectively. With these exceptions the only measurements of soft absorption edges are those of Holweck (1927) with radiation which was not strictly monochromatic. The results of Holweck, though they are very interesting as a preliminary investigation in this field, are for methodological reasons not very accurate. Holweck's measurements include the K absorption limit of the elements 9 (F) to 5 (B) and the $L_{II, III}$ absorption of the elements 18 (A) to 13 (Al). For the last element at $L_{II, III}$, he found 68 volts, corresponding to 181 Å.

The concave-grating method as used in these investigations offers a very simple and at the same time very accurate means for studying X-ray absorption spectra in the soft X-ray region (above 50 Å.). Instead of using the continuous X-ray spectrum, which in this region is extremely feeble, the optical spark spectra from elements giving spectra rich in lines are used.

As an example of the applicability of this method a spectrogram taken by Mr Sanner, M.A., is reproduced in figure 9. As source a spark between copper electrodes was used. As is seen in the upper part, which was exposed without an absorbing screen, the line density is very high in this region, 150 to 200 Å. The lower part shows the effect of introducing an aluminium foil 0·5 μ. thick into the path of the radiation. This is practically completely cut off at 170·5 Å., which represents the L_{III}-absorption limit of Al. This value of the wave-length corresponds to $\nu/R = 5{\cdot}34$, which is in the very best agreement with the value $\nu/R = 5{\cdot}3$ computed from the X-ray emission spectrum of Al.

L_{III}-*absorption of* Al

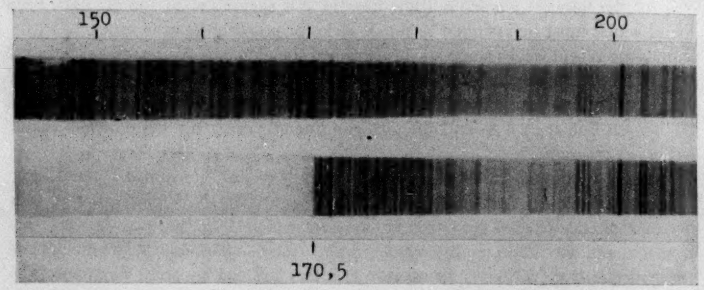


Figure 9. Spark spectrum of Cu-Cu, the lower part with Al-foil inserted. Time of exp. 10 min. and 50 min.

§ 8. ACKNOWLEDGMENT

I wish to thank Mr Torsten Magnusson, M.A., for valuable assistance during the experimental investigations here reported.

535.417 531.715.1

STUDIES IN INTERFEROMETRY—II. THE CONSTRUCTION, TESTING AND USE OF REFLECTION ECHELONS FOR THE VISIBLE AND ULTRA-VIOLET REGIONS

By W. EWART WILLIAMS, M.Sc., Lecturer in Physics,
King's College, London

Received May 25, 1933. *Read July* 7, 1933

ABSTRACT. The practical details of the construction and methods of testing reflection echelons are considered. The various methods of mounting are compared. A method is described whereby the instrument can be used for wave-length measurements. It is further shown that the echelon provides an alternative means of standardizing length units in terms of a wave-length of light.

---

§ 1. INTRODUCTION

When Michelson⁽¹⁾ described the echelon principle thirty-five years ago, he specifically considered the possibility of using the grating as a reflection instrument. The fact that glass transmission echelons can only be employed for the visible and near infra-red regions would be a sufficient reason for using the reflection type. In recent years another real disadvantage of the transmission instruments has become apparent; when a resolving-power of the order of 10^6 is required, as in many hyperfine-structure problems, the transmission echelon becomes so bulky that it is difficult for the optician to mount the plates satisfactorily and for the user to maintain the requisite temperature equilibrium during an exposure.

Michelson foresaw one of the major difficulties in the construction of a reflection instrument, and remarked "Here the difficulty, even supposing the optical work to be perfect, would be the joining of the separate plates in such a way as to have always the same distance between them." Dr C. V. Burton attacked the problem in an entirely different way. Optically plane metal mirrors were separately arranged in echelon formation on a rigid base. Each plate was to be adjusted into its proper position relative to the previous one by means of finely controlled screw adjustments, the correct separation and parallelism being assured by electrical contacts. Dr Burton's untimely death during the War prevented the completion of the task. I was not able to obtain details of his work, and therefore experimented with three Fabry-Perot half-silvered plates. These were adjusted by means of Brewster interference fringes. I was forced to the conclusion that while it would be possible to make the adjustments to the requisite degree of accuracy, I could not think of any design of mount which could reasonably be expected to remain in permanent adjustment. Without this permanency, the large number of plates would require considerable time to be spent in adjusting, and a record would not be trustworthy unless after the exposure the adjustments proved to have been correct. It was with great reluctance that this method was abandoned, since it would be very much less costly than any other, and the plates, once made, could be used again in a different mount to obtain an echelon of different plate-separation.

It has been long known in the optical industry that when two optically plane glass plates are carefully cleaned and freed from dust they will adhere when pressed together. This type of optical contact was first referred to by Twyman(2), and it forms the basis of the optical adhesion described by Parker and Dalladay(3), in which the contacted plates are lightly clamped and are heated in an electric oven to a predetermined temperature. Apart from the heating, the contact is so intimate that no light is reflected at the interface when the plates have the same refractive index. From the measurements of Johnnot(4) on the thickness of the black spot in soap films, it follows that the surfaces are separated by an exceedingly small fraction of a wave-length.

All transmission echelons made in this country since 1908 have been contacted in this way in order to minimize loss of light by reflection at the interfaces. For transmission, the optical criterion is that $(\mu - 1)\, t$ should be constant for each plate, so that small variations in the refractive index μ have to be compensated for by suitable variations in the plate-thickness t. The plate-surfaces are therefore not uniformly plane, so that the optical contact cannot extend over the whole interface. It is however sufficiently general to ensure that the loss of light by interface reflections is small and that the superposed "Fabry-Perot" fringes observed by Stansfield(5) and Kent and Taylor(6) are vanishingly weak.

μ
t

For a period I considered that the sole reason why transmission echelons could not be used as reflection instruments was that these small variations occurred in t, and that if an instrument with plates of constant metrical thickness were to be constructed it would give good definition. Very occasionally, in particularly good meltings of optical glass, the refractive index is so uniform that practically no "touching up" or local polishing of the large plate is necessary. During 1927 a glass echelon of this kind became available. It gave particularly good definition as a transmission instrument, but when it was used as a reflection instrument the results were very poor. Allowance had of course to be made for the fact that the resolving-power and the dispersion were about three to four times greater than in the case of transmission.

The explanation of the discrepancy became obvious when the echelon was tested with the Twyman-and-Green interferometer as described below. The contacting of two plates under pressure causes a slight distortion, which becomes more and more pronounced as successive plates are added. The geometrical echelon formation that is essential seems to make this curvature effect unavoidable since the optical contact has to be obtained by pressure. This curvature has no appreciable effect on the performance of the echelon for transmission work, but makes it practically useless for reflection work. In general, contacted-glass echelons give astigmatic images by reflection.

A solution of this difficulty came accidentally from another investigation in which a Fabry-Perot etalon was crossed with a spectroheliograph(7). Quartz and fused-silica plates were employed instead of glass in order to avoid any distortion due to the heating effect of the comparatively strong beam from the collimator of the spectroheliograph. As it was found extremely difficult to adjust the parallelism of the etalon plates in position on the instrument, I decided to try to contact three plane parallel separators cut from the same strip of fused silica. To my surprise these contacted easily on either the quartz or the fused-silica plate without any pressure being necessary, and the interference rings observed in the neighbourhood of the distance pieces showed no distortional effect. This type of contact in quartz or silica is of a very different nature from that obtained with glass. A glass contact can generally be separated by a sharp blow or gentle pulling of the parts. In this instance it was only with considerable difficulty that the etalon plates could be forced apart; the small separators, measuring 4 × 4 × 3 mm., could only be removed by soaking the plates in petrol for some days, after which they were easily detached.

It was first thought that this improved type of optical contact was entirely due to a greater degree of planeness of the surfaces to be contacted. When a plane surface is being polished the frictional heat makes it convex, and in a great measure the art of the optician lies in working his surface to the requisite degree of convexity so that it will become plane when the temperature is allowed to become uniform throughout the material. This effect is much smaller in quartz and fused silica than in glass for two entirely different reasons. In quartz, the thermal conductivity is approximately twenty times greater than in optical glass, so that the temperature-gradient from the polishing surface is correspondingly reduced; with silica, the almost negligible expansion-coefficient makes the larger temperature-gradient of little importance. Plane surfaces are much more easily obtained with quartz or silica than with glass.

After repeated trials a pair of glass plates which had an even greater degree of planeness than the above-mentioned plates was obtained. Although the glass plates could be cleaned with dilute acid more thoroughly than with quartz or silica plates, an optical contact could not be obtained in this case without pressure. In order to avoid temperature distortion in the handling of the plates asbestos gloves were worn. There seems to be some fundamental difference, for which no explanation can at present be offered, between the optical contacting of glass on one hand and of quartz or silica on the other.

This distortionless contacting of quartz or silica indicated that if plane parallel plates of equal metrical thickness could be constructed, a reflection echelon would become a practical possibility. A rough trial made with a few plates showed that the successive contacting with silica did not introduce any further practical difficulties. Through the co-operation and enterprise of Prof. Takamine in venturing to order an instrument built on these lines from Messrs A. Hilger, it became possible to make a full-scale test of the practicability of the method.

§ 2. CONSTRUCTION

Experience had shown that as far as the avoidance of distortion was concerned, either quartz or fused silica could be employed. With glass echelons the practice has been to work a single large plate as plane as possible, provided it has a uniform retardation $(\mu - 1)\,t$ over all its parts. This plate is then cut into the smaller pieces to form the complete echelon. Single plates of sufficient area cannot be obtained in quartz, and as silica in large plates is never perfectly annealed, small distortions inevitably occur when a larger plate is cut. In both cases therefore the individual plates have to be made singly.

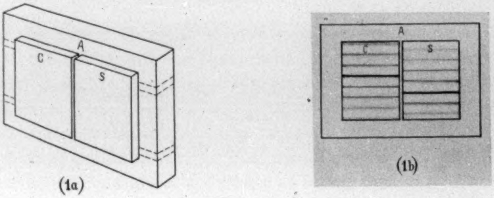
Provided one could be certain that the refractive index was sufficiently uniform, the constancy either of $2(\mu - 1)\,t$ or of $2\mu t$, determined respectively by the Twyman-and-Green interferometer and the Fizeau interferometer*, would suffice to yield the requisite constancy of $2t$ needed for the reflection echelon. It is well known that quartz crystals from different localities have slightly different indices, and it could not be safely assumed without further experiment that the index is sufficiently uniform over the different parts of a single large crystal.

One of the principal difficulties in obtaining long-exposure photographs with transmission echelons is that of keeping the temperature of the echelon enclosure within sufficiently close limits. This difficulty obtains in spite of the fact that the positive expansion of the glass is to some extent compensated for by the temperature variation of the index, which is negative both for glass and air. In most instances some form of thermostatic control must be employed. Other things being equal, the higher the resolving-power of an echelon the closer are the limits within which the temperature has to be maintained. It is by now fairly generally realized that a prismatic spectrograph will never show the same standard of definition, and consequently of resolving-power, when it is used photographically as when it is used visually. This is the case with a spectrograph having a camera lens of sufficient focal length to ensure that the grain-size of the photographic plate shall not affect the definition. The generally accepted explanation is that the prism is subject to minute temperature waves in the material; the resulting small oscillations of the spectral line are recorded as a broadening of the photographic image, and this cumulative effect is not detected in visual observation. This reduction of resolving power in prismatic spectra arises from the variation of the refractive index with temperature, and correspondingly it would occur in a reflection echelon as a result of variation of the plate-thickness with temperature. Hence it is obvious that material having the lowest possible coefficient of expansion should be used, provided it will give the distortionless optical contact that is essential. Invar steel apparently will not contact in this way, so that the plates must be made of fused silica.

The standard of accuracy of workmanship in the reflection instrument is between three and four times higher than that in the transmission instrument when used in the same spectral region. The principal field for the use of the reflection form is the ultra-violet and possibly in the Schumann region, which is as yet unexplored so far as high resolving-power is concerned. A standard at least ten times higher than before has to be aimed at; this implies the taxing of the optician's skill to the utmost, and the development of special methods of testing which would show up the minute errors that are no longer allowable. It was therefore considered desirable that the plates should all have the same area; such a pile would have greater rigidity than the usual wedge-shaped pile, and the increased cost of the material would be more than compensated for by the greater ease and convenience in working and testing the plates. The minimum plate-thickness should not be less than about 4 mm.; thinner plates are liable to distortion in working unless the area of each plate, at present 43 × 36 mm., be reduced. The maximum plate-thickness is primarily governed by the total height of the complete echelon; to ensure the necessary rigidity, the cross-sectional area of each plate should be increased if the total height of the pile exceeds 25 cm.

---

* It will be observed that a determination of the retardations $2\mu t$ and $2(\mu - 1)\,t$ for a plate will give both μ and t implicitly. This method has long been in regular use by Messrs Hilger to determine quantitatively the local variations in the index of a melt of optical glass.



(1a) (1b)

Figure 1.

The plate-thickness of the first instrument was chosen to be slightly greater than 7 mm. This would give one of the main components of H_α, midway between the orders of the other component, so that the separation between these components could be measured without any error due to the Oldenburg *Schrumpfungs Effekt*. This important problem still remains to be finally solved by the employment of adequate resolving-power together with suitable cooling of the light source with liquid hydrogen or helium instead of liquid air.

The silica plates are first roughly cut and ground to the required size and thickness. Originally the long edges were left grey or matt, but as it was found that the matt surface caused appreciable scattering, especially in the far ultra-violet, the long edges in some of the later instruments were optically polished; as a further precaution, in future these edges will be optically worked so that they make angles slightly less than 90° with the working face of the echelon plate. After the polishing process the inevitable differences in thickness between the various plates were determined in the following way.

Two plates S and C, figure 1 (*a*), were placed in optical contact side by side on a larger plate A of quartz or silica, the surface of which was known to be plane. The composite mirror was then set up as one arm of a Twyman-and-Green interferometer, in place of E, figure 2, and the appearance of the field of view was in general as shown in figure 1 (*b*), where the central fringe for C is displaced approximately 1·7 fringes from that of the standard S. A slight downward pressure on the arm carrying the unit causes the optical path in that arm to increase, and if in consequence the fringes also move downwards the plate C is approximately $0{\cdot}8\lambda$ thicker than S. A more accurate value can be obtained by substituting monochromatic radiation for the white light of the interferometer. The different plates were thus measured in terms of the standard S. Finally, the thinnest plate is chosen as the standard and all the other plates were worked down to this thickness by repeated polishing and testing. If by accident a particular plate be polished so that it is thinner than the new standard, either that plate must not be used, or all the other plates must be reworked down to its standard.

The work of contacting, removal for reworking, and recontacting the plate on A is extremely laborious, and attempts were made to reduce the area of contact by employing plane strips or rails, indicated by dotted lines in figure 1 (*a*), instead of a plate. It was found that the thickness of the plates worked by this control steadily increased; each optical contact involves a slight wear of the narrow rails, and in time the wear becomes large enough to be measurable. Messrs Hilger have developed a new type of double interferometer which obviates the necessity for continual recontacting of the plates*. This arrangement has been described by them in detail elsewhere. The writer is at present investigating the possibilities of a modified form of this interferometer which should enable a still higher degree of accuracy to be attained. This will be described in a subsequent paper in this series.

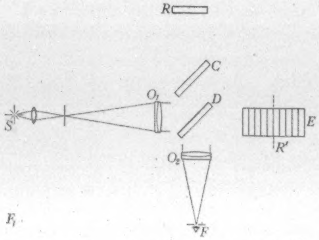


Figure 2. Twyman and Green interferometer test of reflection echelon.

§ 3. MOUNTING

When it is realized that a good optical contact of the type under consideration is nearly as strong and rigid as the material itself, one would not expect appreciable distortion in a pile of the cross-sectional area employed when the length is of the order of 20 cm. Yet if the echelon is supported at its ends with the steps horizontal, the sagging of the centre manifests itself in a considerable change of focus of the diffractional pattern. In accordance with a suggestion made by Mr Twyman the pile rests on narrow fibre strips inside an optically worked rectangular box of invar steel. In this way each plate receives its share of support, and the strip is so thin that no perceptible movement of the echelon in its box can be detected.

---

* British Patent Specification, No. 367859 (Twyman and Dowell).

§4. THE TESTING OF REFLECTION ECHELONS

The performance of a line grating, a Lummer plate, or even a transmission echelon can be immediately tested by examining the definition of the patterns obtained for spectral lines from selected sources. One knows from long experience what standard should be obtained with the green mercury radiation if the workmanship be sensibly perfect. The resolving-power of a large reflection echelon is, however, so high that this direct test is much more a test of the pressure, temperature, and current-density in the mercury lamp than of the instrument. It is quite probable that a systematic search would lead to a critical resolving-power test, in the same way that the clean resolution of the Fe triplet at λ 2749 Å. is at the present time regarded as a critical test for a large back-reflecting quartz spectrograph (E 1).

A test of this nature, if not satisfactorily passed, yields little information as to the nature of the defect and the position of the defective plates, so that a more direct method is highly desirable if not essential. The first method adopted is shown in figure 2. The echelon *E* was mounted as one mirror arm of a Twyman-and-Green interferometer and the green radiation from the mercury source *S* was selected by placing a suitable filter at *F*, the focal plane of the second objective O_2. The successive steps (1 mm. at a distance of about 100 cm.) were rather difficult to see clearly, so that either a magnifying field lens (not shown in the diagram) was used, or a special short-focus lens was substituted for the standard 60-cm. objective O_2 and the echelon was mounted as close to the dividing mirror as possible. The reference mirror *R* was adjusted so that its image in *D* coincided with one of the step faces of the echelon.

When the image *R′* makes a small angle with the echelon step in the horizontal plane, the pattern observed in the field of view is that shown diagrammatically in figure 3 (*a*). Since $2t$ will not in general be an exact integral multiple of the mean wave-length of the central part of the green line, the fringes from successive steps will not be coincident.

A wide variation in the clearness or the visibility of the fringes from the different steps is immediately apparent. If the image of the reference mirror practically coincides with, say, the twelfth step, the fringes here are most distinct, while those of the eleventh and thirteenth steps are only slightly less clear. The falling off in the visibility of the tenth and fourteenth-step fringes is more marked, and after the eighth and sixteenth steps the fringes are too ill defined to be seen with certainty.

By suitably tilting the reference mirror *R* the now inclined fringes can be made to run into each other as shown in figure 3 (*b*). The resultant composite fringe is however, not straight, but has the *S* formation shown in figure 3 (*c*). The immediate deduction was that the plates were distorted; that while plates 11, 12 and

13 were sufficiently uniform, 8 and 15, and still more 9 and 16, had different values of effective plate-thickness. This interpretation was proved to be incorrect by displacing the reference mirror so that its image coincided with the ninth step. While the eighth, ninth and tenth-step fringes were now in line, the fringes in the eleventh, twelfth and thirteenth steps were curved to the right as in the upper part of the ∫ sign, but the fringes in the same three steps were curved in the opposite direction when the reference mirror was moved so that its image coincided with the fifteenth step. Thus this curvature was independent of the echelon and arose simply because of the asymmetry of the intensity-distribution in the green-line source. The red radiation from a Michelson cadmium lamp was then tried as a source. This is much less bright than the mercury light, and in this type of interferometer, where the light from a pinhole has to be spread over the whole field of view, the fringes were extremely faint, but as far as one could tell the composite fringes appeared to be straight.

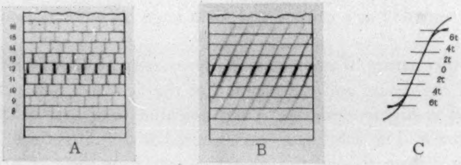


Figure 3.

It will be realized that a photograph of these composite fringes from a perfect interferometer and echelon would suffice to give the visibility and phase curves required to determine uniquely the distribution of an asymmetric spectral line*. The visibility data could be obtained from microphotometer curves of the fringes in the various steps and the phase curve by measuring the deviation of the outer fringes of the outer steps from the alignment set by the central-step fringes. As a method this is only of academic interest, since the available resolving-power would only be that of the echelon itself, which will give objectively all the information that would have to be deduced by a Fourier analysis from the above-mentioned data.

The above experiment has been described in detail since it is almost identical in principle with that of a method devised by Kösters⁽⁸⁾ for standardizing the metre. In his method a ┌─┘-shaped gauge is substituted for the echelon E in a Twyman-and-Green interferometer as in figure 2. The reference mirror image is placed midway, so that the arrangement is equivalent to bringing steps 8 and 16 of figure 3 (*a*) into juxtaposition. It will be obvious that the phase displacement of the fringes due to any asymmetry of the line source will be doubled and can introduce a systematic error far in excess of the possible errors of observation. These phase displacements have long been known and studied by metrologists, but the simple interferometer, whether of the Michelson or of the Twyman-and-Green type, only enables the *difference* between the phase curves of any two sources to be determined. It appears to the writer that results obtained by this method cannot be relied upon unless also the spectral line employed can be shown to be symmetrical to the required degree of accuracy. The same criticism will apply to some extent to wavelength measurements with Fabry-Perot interferometers with lightly silvered or platinized surfaces, in which the poor reflecting coefficient of the films is apparently compensated by the use of a high order of interference. A fairly close analogy would be afforded by the problem of finding the position of a variable binary star by means of a telescope. With a small objective aperture the diffractional image would appear symmetrical, with the centre of light-intensity of the binary as the axis. As the aperture is increased the pattern becomes more and more asymmetric, but the true positions of the components cannot be found until they are cleanly resolved, since they may differ both in magnitude and in intrinsic brightness.

---

* Michelson, *Studies in Optics*, pp. 39, 40.

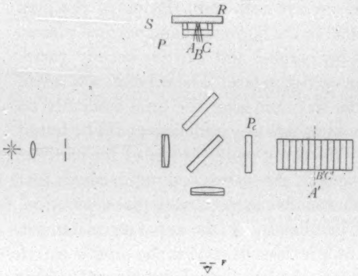


Figure 4. Combination of Fabry-Perot and reflecting echelon in Twyman-and-Green interferometer.

The following method, shown in figure 4, was devised to eliminate the possibility of spurious results arising from asymmetry of the source; it functions almost equally well with a white light source. The silver was removed from all but the centre portion of the plane quartz reference mirror *R*, and the two halves of a spare echelon plate *S* were contacted to it. A plane parallel quartz plate *P* was lightly silvered and contacted to the silica separators, the silver being carefully removed from the parts of *P* to be contacted to *S*. The unit then formed an interferometer similar to that of Benoit, the precursor of the arrangement of Fabry and Perot, but in the latter the fringes are observed by transmission instead of by reflection, as in the original Benoit method. This unit was mounted in place of the movable mirror in the Twyman and Green interferometer, and a compensating plate P_c of the same optical thickness as *P* was added to the echelon arm as shown.

The unit was adjusted until the image of the silvered surface *R* coincided with the plane of one of the steps *A*′. The usual white-light fringes could be seen in that step; a similar set in the next step *B*′ was given by the light which had undergone one internal reflection in the mirror unit, while the fringes in *C*″ corresponded to two such reflections. If the optical-path difference of the unit (allowing for the effect of phase changes at reflection) is equal to twice the plate-thickness of the echelon, the fringes will be in alignment and the appearance of the field of view will be that shown in figure 5. The separators were cut from a slightly thinner and therefore useless echelon plate. By chance this happened to compensate almost exactly for the phase-change at the inner surface of P, so that the fringes from the consecutive steps were in line. The fringes rapidly decrease in clearness, so that at the fifth step only the central (zero-order) fringe can be seen. This decrease is due in this case to the fact that while the amplitude of the wave reflected at the various echelon steps is constant, that reflected from the unit decreases rapidly with each multiple reflection. Any lateral displacement of the fringe system at any one step would show that step to be either too thick or too thin. A variation in the separation of the fringes would mean that the plate was not parallel. By tilting the movable unit, the fringes could be arranged so that only a single horizontal zero-order fringe appeared in each step. Provided the step faces are strictly parallel in the horizontal and vertical planes, these fringes should be parallel and occupy exactly corresponding positions in each step face. The echelon was tested every five steps in this way, and after the final assembly no detectable displacement or lack of parallelism could be found in any of the steps. This is not merely a test of the metrical equality of the plates but of the real optical requirement that the surfaces of the consecutive steps have equal separation. If the equality and parallelism of the separate plates are definitely assured from previous tests with the double interferometer, this becomes a test of whether the optical contacting of the plates has been uniformly successful.

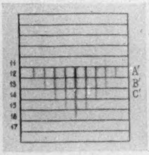


Figure 5.

Neither of these tests provides a means of guarding against another possible source of error—a uniform variation in the plate-thickness which, while imperceptible in two or three successive steps, might amount to an appreciable fraction of a wave-length in a complete echelon of 30 to 40 plates. If the separators of the etalon unit were made five times thicker than the echelon plates, white light fringes would be visible at the first, fifth, tenth, etc. plates, and this result would prove the absence of any uniform variation. Fortunately this was not necessary since the primary effect of a uniform variation in the optical-path difference is to cause a change of focus of the image. This can become comparatively large before the standard of definition is appreciably reduced. This point has been discussed by Twyman(2) in connexion with the effects of clamping pyramidal transmission echelons and is further exemplified by Koláček(9) in an analysis of slightly wedged-shaped Lummer plates. Some difficulty due to this effect was at first experienced when the echelon was tested in its mount. Instead of coming to a focus at the focal plane of a 170 cm. objective, the pattern was focused about 5 mm. beyond; the definition appeared as good, however, as when the echelon was tested without its mount, in which case the pattern was correctly in focus at the focal plane of the lens. An alteration in the design of the mount enabled this error to be reduced to a fraction of a millimetre.

§ 5. EFFECT OF IRREGULARITIES IN THE STEP-WIDTH

For an echelon of step-width s and plate-thickness t, the separation between consecutive edges k is $(s^2 + t^2)^{\frac{1}{2}}$. If α and β are the angles of incidence and diffraction as measured from the normal to the diffracting surfaces, the angles of incidence and diffraction measured from the normal to the plane containing the edges of the echelon steps are $(\gamma + \alpha)$ and $(\gamma + \beta)$. From the simple theory of the line grating, the path difference between beams from consecutive steps is:

s

k, α, β

$$k\,\{\sin(\gamma + \beta) + \sin(\gamma + \alpha)\} \qquad \ldots\ldots(1).$$

Since $\sin\gamma = t/k$, and $\cos\gamma = s/k$, the equation for reinforcement becomes:

$$t\,(\cos\alpha + \cos\beta) + s\,(\sin\alpha + \sin\beta) = m\lambda \qquad \ldots\ldots(1a).$$

m

The incident and the diffracted beams invariably make very small angles α and β with the reflecting step face, so that the expression, without any appreciable loss of accuracy can be further simplified into

$$2t + s\,(\alpha + \beta) = m\lambda \qquad \ldots\ldots(2).$$

s should be constant as well as t, since a change δs in the step-width will cause a variation $\delta\beta$ in the angle of the diffractional maximum given by

$$\frac{\delta s}{s} = -\frac{\delta\beta}{(\alpha + \beta)}.$$

If a spectral line is in single-order position $\alpha = -\beta$, and no loss of definition due to any variation of s, however large, can occur. In double-order position $(\alpha + \beta) = \lambda/2s$, since λ/s is the angle between the orders, while for the outer orders, if visible in this position, $(\alpha + \beta) = 3\lambda/2s$; the tolerances that are allowable in s to secure sensibly perfect definition of the central orders must be reduced threefold if the same standard is to be maintained for the outer orders.

That small variations of the step-width do exist can be easily seen by direct inspection, and the effect is even more prominent in glass transmission instruments where the contacting is more difficult to achieve. The effect was studied in some detail with the third and fourth instruments, using a water-cooled quartz mercury lamp (Hansen type) as a source. In neither case could any difference be detected in the standard of definition of a component when it was changed from single to double-order position. On the other hand, the definition of the outer orders was invariably inferior to that of the central orders. It would be a great convenience in rapid working if these orders could be utilized. The centre of gravity of a somewhat broad line or an unresolved group is spuriously displaced by the instrument when the line is in double-order position. This is due to the fact that the amplitude curve for a single slit varies rapidly at these positions, while those of the outer orders nearly coincide with the positions of the secondary maxima and are not perturbed by this effect. Suppose, for example, that the pattern consists of one or two weak lines placed approximately midway between the orders of a much stronger group. The weak lines could be examined in single-order position, and while the double-order image of the strong group may be much over-exposed, the outer orders of this group would be at a suitable intensity for measurement. The writer intends to try the experiment of measuring the step-widths of an echelon with a travelling microscope or cathetometer and to mount ┌─┘-shaped diaphragms on the sides of the steps. These diaphragms can be machined to the requisite dimensions for each individual step, so that all the apertures have both uniform width a, and uniform lateral spacing s. It is only when the gap or obstructing part between any two consecutive steps is small compared with the width of a reflecting face that the instrument behaves as a true echelon. When a line is in double-order position, the angles that the various orders make with the normal to the step face are $\pm 0{\cdot}5\lambda/s$ and $\pm 1{\cdot}5\lambda/s$. The maxima for a single slit occur at 0 and $\pm 1{\cdot}43\lambda/a$. These values will also be correct when the light is incident on the grating at a small angle α, provided the direction $-\alpha$ is taken as the axis for measurement.

If the obstruction be chosen so that $1{\cdot}43s = 1{\cdot}5a$, the outer orders of a line in double-order position will coincide with the point of inflection of the amplitude curve of a single slit, and a somewhat broad line in this position will not be spuriously displaced.

In an experiment to test the practical importance of this point a high-pressure neon tube was used as a source, so that all the lines were somewhat broad. It was found that the distances between the inner orders of lines in double-order positions were approximately 1 per cent less than a third of the corresponding distances between the outer orders. In a similar test with a sharp satellite of the green Hg line no difference could be observed.

§ 6. CONSTANT-PRESSURE CHAMBER

It has long been known that extended exposures with the Fabry-Perot interferometer, for example, are frequently unsuccessful because of variations in the pressure of the atmosphere during the exposure. If an accuracy of 0·001 Å. is required for a wave-length 5000 Å., the variation of the atmospheric pressure during an exposure must not be such as to produce a variation of 1 part in 5×10^6 in the refractive index of the air. This corresponds approximately to a pressure-difference of 0·5 mm. of mercury, a difference that occurs only too frequently in a long exposure over a few hours. Even with an ordinary line grating this effect is a source of trouble and Merton⁽¹⁰⁾ has devised an ingenious scheme whereby the effects of temperature-variations and pressure-variations can be cancelled during the exposure by means of a relay which introduces or removes an auxiliary heating system to compensate automatically for them. When still higher accuracy is required, the pressure-tolerances are correspondingly reduced; thus Perard⁽¹¹⁾ has recently given the mean wave-length of one of the krypton lines to the fifth decimal place in Ångstrom units. For this to have an absolute physical meaning, the pressure should be constant and specified to within 0·005 mm. The permanency associated with such optically contacted etalons and reflection echelons would enable these instruments to be placed *in vacuo* and this would also reduce any temperature disturbances. This idea was incorporated in a patent specification⁽¹²⁾ filed on June 11, 1928.

In the initial tests of the first instrument an apparent disadvantage of the reflection form was encountered. The change from single to double-order position for the transmission type can be easily effected by a small tilt of the instrument so that the optical retardation of a plate can be increased by half a wave-length without alteration of the direction of the transmitted beam. In the reflection instrument only half this tilt is required, but the reflected beam is now deviated out of the field of view. This point could hardly have been foreseen, since no measurement of the tilt angle is normally made with the transmission instrument. Mr Twyman* at once proposed, in a letter dated October 26, 1928, to vary the pressure in order to change the order positions. He stated that this plan was suggested by consideration of the vacuum etalon, and he calculated the pressure differences required. He pointed out in his letter that since the density of the air would remain unaltered, its refractive index would not change and a small variation of temperature would be immaterial owing to the smallness of the expansion coefficient of silica. The method when tried proved very successful, and with it, extended exposures could be relied on to give as good definition for the weaker lines as were given by the short exposures for the stronger sources.

§ 7. METHODS OF USING REFLECTION ECHELONS

The obvious way to combine a reflection echelon with the necessary auxiliary dispersion system is to use the echelon as the mirror in a back-reflecting, Littrow type of spectrograph. Thus, if the reflecting film on the back of the quartz prism of the Hilger E 1 spectrograph be removed the echelon can be mounted behind the prism, and such an arrangement would be most compact and economical of light. This method was originally contemplated during the construction of the first instrument, but during the testing the disadvantages of the arrangement became apparent.

When an autocollimating telescope with a horizontal slit is used to observe the diffraction fringes from the echelon, it will be seen that while the fringes are horizontal at the end nearer the slit, towards the edge of the field the fringe curves downwards or upwards, according to whether the echelon stair ascends or descends away from the objective. If θ is the angle which the incident beam makes with the normal to the step faces of the echelon in the horizontal plane (i.e. with a line parallel to the long edges of the step apertures) equation (2) has to be modified into:

$$2t \cos \theta + s(\alpha + \beta) = m\lambda \qquad \ldots\ldots(3),$$

which may be rewritten

$$2t(1 - \tfrac{1}{2}\theta^2) + s(\alpha + \beta) = m\lambda.$$

For any given fringe, since the incidence angle α is constant,

$$(t\theta^2/s - \beta),$$

should be constant.

---

* This detailed explanation is given because D. A. Jackson, *Proc. R.S.* A. **128**, 508 (1930), has described the echelon and pressure chamber without any acknowledgment other than that the echelon was made by Hilger's. The complete patent specification was filed on March 8, 1929 and accepted on May 30, 1929.

The slope $\partial\beta/\partial\theta$ of the fringe

$$2t\theta/s \qquad \text{......(4).}$$

This simply means that if the light is incident obliquely on the echelon edges, the reduced path difference is compensated for by a larger diffraction angle as measured from the normal of the plane containing the edges of the steps. The same effect should occur with ordinary line gratings, but much larger skew angles would have to be chosen before the effect became apparent. In the echelon the ratio t/s is about 7 while in the line grating it is of the order of unity.

Only in a few cases would it be practical to have the dispersions of the spectrograph and the echelon parallel, so that in general the dispersions must be crossed. In the usual quartz spectrograph such as the Hilger E 1 the slit is effectively at the side of the plate. If a reflection echelon be used as a mirror behind the prism, the light falling on it must make increasing angles in the horizontal plane as the wavelength decreases. With a horizontal cross slit, the echelon fringes become more and more inclined, in accordance with equation (4). It can be easily shown that as the slope becomes pronounced the available resolving-power is correspondingly reduced.

Suppose we consider a point P on the narrow horizontal slit, illuminated by monochromatic light, the central diffractional image seen with the echelon steps horizontal will be a rectangle $ABCD$, figure 6, the angular width of AC in the direction of the dispersion being $2\lambda/Ns$ while in the horizontal direction AB has an angular width $2\lambda/h$, where h is the length of the step. Another point Q on the slit will have as its image the rectangle $EFGH$, which is displaced upwards through the angle $\delta\beta$ on account of the variation in θ. Other points, between P and Q on the slit, will have their rectangular diffraction patterns between these rectangles. The resultant fringe is therefore contained between AH and DF, and the angular width of the fringe in the direction β of the dispersion is proportional to DH instead of to AC. With a slope $\partial\beta/\partial\theta$ the angular width of the fringe is increased in the ratio HD/AC, and the resolving-power is reduced in the inverse ratio. It will be seen that

h

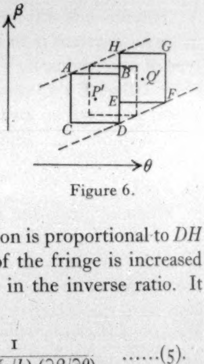


Figure 6.

$$\frac{\text{resolving-power when } \theta=\theta}{\text{resolving-power when } \theta=0}=\frac{AC}{HD}=\frac{1}{1+(2Ns/h)\,(\partial\beta/\partial\theta)} \qquad \text{......(5).}$$

If we assume that we are prepared to accept a 10 per cent reduction of the resolving-power, the maximum permissible value of $\partial\beta/\partial\theta$ according to equation (5) becomes $h/18Ns$. Substituting this value in equation 4, the maximum value of θ should not exceed $\bar{\theta}$ where

$$\bar{\theta}=h/36Nt \qquad \text{......(6).}$$

This being the angle of incidence on the horizontal plane, the beam falling on the photographic plate will make an angle twice as great with the incident beam, so that the total angular range θ over which the resolving-power is not reduced by more than 10 per cent is $h/18Nt$. For reflection echelons of plate-thickness 0·73 cm., and height 4·0 cm., this angle only amounts to 40′ in a 25-plate echelon and 25′ with a 40-plate instrument.

The width of the aperture perpendicular to the axis of the quartz lens of the standard E 1 spectrograph varies from about 8 cm. to 12 cm. according to whether the spectrograph is set for the first (visible) position or the fourth position for the lowest wave-length region. If the lens had been achromatic so that the plate is normal to the axis, only the patterns in the first 2 cm. or 1·3 cm. of the plate nearest the slit would have the required standard for a 25-plate or a 40-plate echelon. Table 1 gives the approximate lengths of the 25 cm. plates over which the resolving-power should be 90 per cent or higher.

Table 1

Focal length of objective (cm.)	Number of plates in echelon	Useful length of plate	
		First position visible (cm.)	Fourth position (cm.)
170	25	6·0	4·0
	40	4·3	2·9
300	25	10·6	—
	40	6·5	—

The complete range of the E 1 instrument is usually obtained in four settings; with this method of using the reflection echelon at least 20 positions would have to be determined with a 25-plate echelon, and correspondingly more for more powerful instruments. If a 300-cm. objective be used in place of the 170-cm. lens with a 40-plate echelon, about 50 positions would have to be standardized with reference to lens, prism-position and plate-tilt.

If the spectrograph were redesigned so that the slit lies either above or below the axis of the lens, the above ranges would be automatically doubled. In the above calculations it has been assumed that the slit is in effect at the exact edge of the plate. Since the totally reflecting prism is a few centimetres distant from the slit, allowance has to be made for the spread of the beam so that the extreme edge of the plate does not correspond to the zero angle of incidence on the echelon, as it has been assumed to do for the purposes of the above table.

A further defect of this arrangement, that has not been fully investigated, arises from the fact that the slit is placed to give a parallel beam on the prism for the wave-lengths corresponding to the centre of the plate. For wave-lengths at each end of the plate, the slit is approximately ± 10 cm. beyond the focal plane, and the beam incident on the echelon is not parallel. With a 170-cm. objective the planes of the images focused by the extreme steps of a 40-plate echelon differ by ± 1·3 mm. from that reflected by the central step. This is much more than the experimental depth of focus with a 4-cm. aperture so that the light from the outer steps is effectively spread over a larger horizontal strip and these steps do not contribute their full quota for interference purposes. The resolving-power is thereby lessened in the same way as in the case of the Lummer plate. The main disadvantage of this effect is that it is at a maximum at the end of the plate, which, according to the above table, is the only part that can be employed to give approximately full resolving-power. If by means of an extension tube the slit were moved 7 cm. outwards and the lens were suitably displaced, the beam incident on the echelon would be sufficiently parallel for that portion of the plate which can be usefully employed.

A further disadvantage of this type of mounting is that it cannot be employed for standard wave-length measurements. This, in the writer's opinion, is probably the most important function of the reflection echelon, since for general hyperfine-structure work two or three such echelons of different plate-thickness should be available, so that the effect of overlapping orders can be avoided.

For these reasons, this method was abandoned and the principle of projecting the echelon pattern on the slit of the spectrograph adopted. This involves considerable loss of light in the extra reflection and refraction surfaces involved, and increased difficulties in coupling two separate instruments, but the advantages far outweigh the disadvantages.

Either a lens or a concave mirror can be employed to project a parallel beam on the echelon and to bring the diffracted beam into focus on the slit of the spectrograph. The mirror method is free from all difficulties of chromatic aberration, and although it does not permit as adaptable a mounting as the lens it would be much easier to construct; the reflecting-power of platinum in the ultra-violet is only about 33 per cent, and since two such reflections have to occur the final image will have an intensity of approximately $\frac{1}{9}$ of that possible when a lens is employed instead of a mirror. For that reason alone, in view of the necessity for collecting all the light possible, the simpler mirror system was abandoned for the more difficult lens method*.

Figure 7 shows a diagrammatic side view of the arrangement. The light from the horizontal slit S_1 is totally reflected by the prism P and emerges from the lens L as a parallel beam. The light diffracted from the echelon E is in turn focused across the vertical slit S_2 of the spectrograph, which makes a coarse analysis in the horizontal plane. With a properly constructed echelon the definition is equally good over the whole of the plate provided that the lens L is sufficiently achromatic. A quartz-fluorspar doublet was originally used but proved insufficiently achromatic, and a quadruple lens of quartz-fluorspar-sylvine-quartz has been designed by Mr Perry(14) of Messrs Hilger. In this objective the thickness of each component has been chosen with the object of reducing the chromatic aberration, the values of which are shown in curve *b* of figure 8. Curve *a* is that of the quartz fluorspar doublet. It might be remarked here that the construction of such an objective

---

* Since this was considered, Hocheim has developed a method of obtaining a high-reflection-coefficient mirror in this region and Ritschl(13) has employed a Hocheim mirror instead of a lens. The reflection coefficient falls off very abruptly at 2300 Å., long before the limit for quartz is reached.

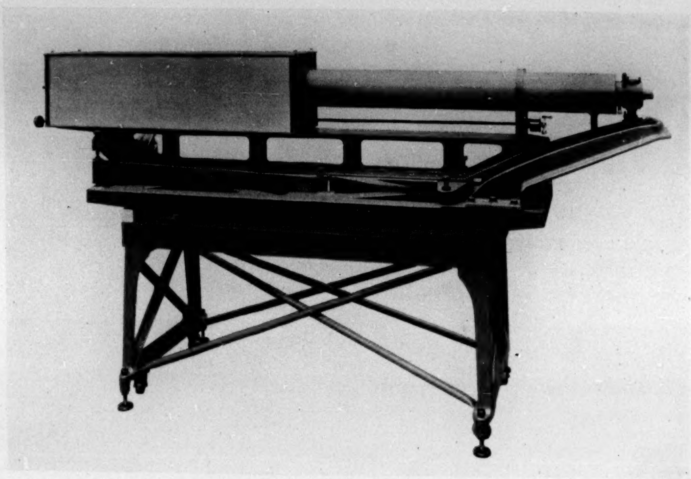


Figure *A*.

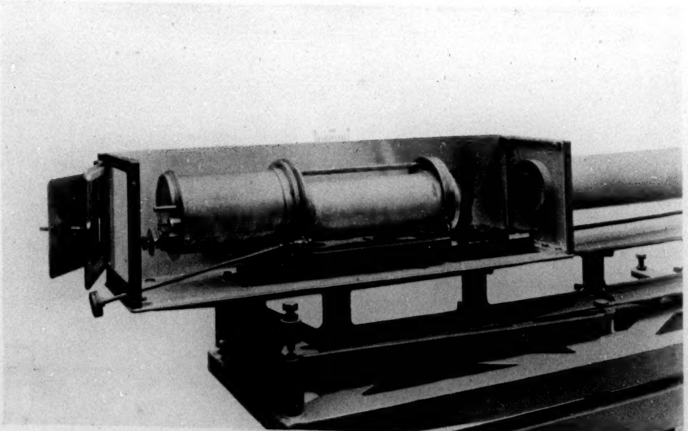


Figure *B*.

represents a wonderful technical achievement in lens-making. As homogeneous fluorspar of the required dimensions is not available, this component has to be constructed from a plate made up from four or five pieces, each of which has to be carefully cut to shape, and the pieces are cemented together to form a plate before being ground and polished to the lenticular form. The cement must be sufficiently rigid to prevent even a minute relative movement of the separate parts, while it must be sufficiently elastic to avoid accidental double refraction in the easily strained fluorspar. To yield critical definition the lens must be carefully centred, and adjustments for this purpose are included in the lens-holder.

The problem of mounting plates has been solved by using a substantial box of invar steel; they are held in position by four thin plates which touch them at the edges only, and a small amount of end play is allowed. The ends of the box are enlarged to carry two adjustable mirror strips, the purpose of which is explained in the next section. These ends also have four set-screws and, the framework being standardized, different echelons can be used in the same pressure chamber *C*. The pressure was originally measured by means of a tubular gauge containing a globule of mercury, but this tarnished in the course of time and tended to move jerkily when the pressure was uniformly varied. A pressure-gauge working on the principle of the aneroid barometer with a 360-degree scale corresponding to pressures of from 0 to 50 mm. has been substituted in the more recent instruments. An auxiliary pressure or vacuum chamber *P*, connected by means of a needle valve, allows the pressure in the echelon chamber to be varied without the whole having to be connected to a pumping system.

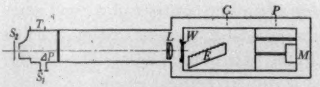


Figure 7.

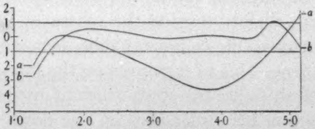


Figure 8. Residual chromatic aberration for $F = 1000$ mm. The ordinates give the variation of the focal length in mm. The abscissa is the corresponding wave number $\times 10^{-4}$.

In order that the full advantages of a reflection echelon may be obtained it should also be possible to use it so that its dispersion can both assist and oppose that of the auxiliary spectrograph. In the absence of another high-resolving-power instrument or another echelon of slightly different plate-thickness this forms the only available method of deciding whether a satellite lies on the long or short-wave-length side of a main line. For this reason the chamber unit is made in a cylindrical form and mounted on four rollers so that it can be rotated by means of an adjusting-rod, the pinion of which engages in a cogged wheel that forms part of the chamber. Friction brakes at the sides prevent the chamber from rotating too easily. The head carrying the slit and the reflecting-prism can be rotated so that the slit can be placed either above or below or at either side of the collimator tube, the exact positions being fixed by means of a spring plunger. This has proved a great convenience in practical work and it is unfortunate that it cannot be applied when a mirror mount is used.

If a relative movement of the two instruments can occur, owing to vibration, a corresponding loss in definition will be experienced. Any attempt to obtain the necessary rigidity by mounting the two instruments on piers on a common concrete foundation would limit their use according to the nature of the auxiliary apparatus needed in connexion with the light source, such as liquid-air or liquid-hydrogen cooling. If the base of the auxiliary mount pivots about a point immediately below S_2, figure 7, the mount can swing in any direction by a considerable amount without displacement of the fringes on the slit S_2. This method has been adopted. A rigid ball-and-socket bracket is clamped to the spectrograph, and one end of the base rests on this while the other two points of the support are slightly outside the centre of gravity of the whole system. The mounting carrying the collimator tube, lens, and echelon chamber consists of a rigid girder frame. This in turn rests on the top point of a vertical triangular casting, the base of which has two studs which fit into grooves in the base of the mount. The chamber end of the girder rests on two projections on a similar vertical casting to which a long horizontal arm is attached. The end of this arm is held to the base by a spring and screw. When the screw is turned, the girder carrying the optical parts moves horizontally either towards or away from the spectrograph. This adjustment, the design which is due to Mr Dowell, is necessary if a parallel beam is to fall on the echelon. The position of the lens L is then fixed by that of the first slit. The whole instrument can be moved by means of this adjustment so that the slit S_2 of the spectrograph is at the focal plane of the lens L. It has been found a great convenience to mount both the instruments on substantial trolleys with clamping bolts which are used when the instruments have been wheeled into position. It is experimentally found that long exposures of 10 or 15 hours for weak lines show nearly as good definition as the short exposures of 5 or 10 minutes required for the stronger lines in the mercury arc. The general appearance of the mounting can be seen from Figure *A* in the plate. Figure *B* shows a side view of the echelon and pressure chambers in position.

The question of the optimum value of the focal length of the lens is a matter of some difficulty. With the 170-cm. focal length the distance between the orders is about 1 mm. in the red, the separation becoming correspondingly smaller as the wave-length is decreased. It is highly desirable to use soft gradation plates, not only on account of their speed but also for the fact that faint satellites are more easily seen on them. Unfortunately such plates have large grain-size, and unless the separation of the orders is about 2 mm. this effect will influence the practical resolving-power obtained.

If only the more intense lines are to be examined, a lens with a 3-metre or even longer focal length might be employed. The intensity would be approximately four times weaker than with the 170-cm. objective, and many lines which can be photographed with the latter would become impossibly weak. The numerical aperture ratio of the E 1 spectrograph is in the neighbourhood of $f/30$, and is sufficiently low for most spectra when the high dispersion of the echelon is considered. It is suggested that when intense lines in the ultra-violet have to be examined with the maximum available resolving-power, a concave mounting on the lines described by Ritschl(13) can be employed. The astigmatism of the mirror becomes negligibly small for a large radius of curvature, since the necessary tilt is reduced.

The mounting described above appears to constitute the best compromise when light-intensity as well as accuracy has to be considered.

§ 8. WAVE-LENGTH DETERMINATIONS BY MEANS OF THE REFLECTION ECHELON

The general method has already been briefly described in a letter to *Nature*(15). Two platinized mirrors with adjustable surfaces are mounted, one on either side of the echelon stair. Their length is equal to the total width of the echelon steps and their breadth is about 5 mm. They are adjusted so that the pattern on the photographic plate, with a wide spectrograph slit and the echelon steps horizontal, is as shown diagrammatically in figure 9. A_1 and B_1 are respectively the $(m_1 - 1)$th and m_1th orders for a known wave-length λ_1. C_1 and D_1 are images of the primary slit S_1, figure 7, reflected by the above mentioned mirrors. Correspondingly A_2, B_2 are the orders for another known wave-length λ_2, while C_2, D_2 are the mirror images for this wave-length. Since the various mirror images correspond to identical points on the spectrograph slit S_2, the path difference of the light diffracted from the echelon to one of these points would be constant. The order of interference at C_1 would be $(m_1 + f_1)$, where f_1 is the fractional part represented by the ratio C_1B_1/B_1A_1. Similarly, that for λ_2 is given by the ratio C_2B_2/B_2A_2. If a line such as λ_3 is in single-order position the separation of the orders cannot be measured, but if the separation for another wave-length λ_1 is known it can be calculated since f_1

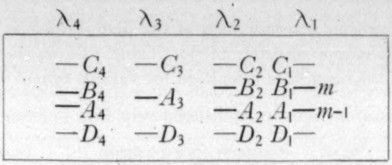


Figure 9.

$$\text{order separation for } \lambda_3 = A_1B_1 \frac{\lambda_3}{\lambda_1} \times \frac{C_3D_3}{C_1D_1}$$

and the fractional part f_3 will be C_3A_3 divided by this quantity.

We then have

$$(m_1 + f_1)\,\lambda_1 = (m_2 + f_2)\,\lambda_2 = (m_3 + f_3)\,\lambda_3,$$

and the accurate values of $f_1, f_2, f_3, \lambda_1, \lambda_2, \lambda_3$, and the approximate value of m being known, the exact value can be quickly found, and the product $(m_n + f_n)\lambda_n$ is determined to an accuracy depending on the accuracy with which the standard wave-length and its fractional part are known. If the wave-length of a fourth line λ_4 is sufficiently known, so that there is no ambiguity in the value of the integer m_4, a determination of f_4 will enable the wave-length to be obtained to a much higher degree of accuracy. Table 2 shows a typical measurement and calculation for a number of neon lines with a 25-plate echelon. These were made by Mr Rymer at this laboratory. He had had no previous experience in plate measurements.

The echelon chamber was evacuated, so that the vacuum wave-lengths of the neon lines had to be calculated from Meggers and Peters's formula. The vacuum wave-lengths of red cadmium has been taken as 6440·2513 Å., this being the provisional value recently determined by Sears and Barrell(16).

Table 2.

Wave-length in air	Wave-length in vacuo	Observed fractional part
6438 Cd	6440·2513	0·973
6717 Ne	6718·896	1·374
6598 Ne	6600·774	0·997
6532 Ne	6534·686	1·560
5975 Ne	5977·185	1·165

From the micrometer determination of the plate-thickness the order of interference for 6438 Å. is approximately 22630. Table 3 shows the various orders and fractional parts of the neon lines calculated for various orders of λ 6438.

Table 3.

Wave-length	6438	6717	6598	6532	5975
Observed	0·973	$0·37_4$*	$0·99_7$*	$0·56_0$*	$0·16_5$*
	22654·97	21715·43	22104·03	22327·58	24410·11
	22655·97	21716·38	22105·01	22328·56	24411·18
	....	....	....	....	....
	22656·97	21717·34	22105·98	22329·55	24412·26

From the agreement of the calculated fractional parts of the middle row with the experimentally determined values given above it is evident that this is the correct order, so that the effective path difference for this instrument is 1·45910140 cm. This is very closely twice the thickness of the echelon plate.

Wave-length measurements with the reflection echelon in this manner appear to have very marked advantages over the corresponding determination with the Fabry-Perot interferometer. The primary advantage is that the resolving-power as measured by the sharpness of the fringes is independent of the wave-length, while the reflecting-power of the metallic films of the Fabry-Perot instrument decreases rapidly in the ultra-violet region. A practical advantage is that the determination of the fractional part can be made in much less time than the corresponding determination with the Fabry-Perot instrument; this is of importance when a large number of lines have to be measured. No account need be taken of the variation with wave-length of the phase-change at reflection, and the instrument remains in permanent adjustment. By making the determination in vacuo all the corrections for atmospheric temperature, pressure, humidity, and carbon-dioxide content of the air are eliminated, and the wave-numbers are obtained directly without recourse to any refractive-index tables.

---

* The neon tube employed gave somewhat broad, unsymmetrical fringes due to an incomplete resolution of the isotope displacements. The measurements show that the inclusion of the third decimal for the fractional part is not justified in this instance and is only given as an indication.

This method enables the absolute wave-number of any satellite to be determined with somewhat better accuracy than the difference between its wave-number and that of its main line, since the latter may be somewhat broader while the reference points for the sharper satellite are the extremely sharp reference mirror images and the orders of the standard line.

A 40-plate echelon now under construction should be able to resolve two lines of equal intensity which have a separation of 0·018 cm^{-1} independently of their position in the spectrum. The wave-number difference corresponding to a whole order is 0·720 cm^{-1}, so that the wave-number of a sharp line should be obtained to within 0·001 or 0·002 cm^{-1}.

It is well known that owing to the character of the intensity-distribution curve in echelon spectra, the centres of gravity of the two orders of a somewhat broad line are spuriously displaced towards each other. Merton and Barratt(17) have given a method depending on the measurement of the width of the line in single and double-order position whereby this displacement can be evaluated.

The following method will give this quantity more directly. If we write κ for the

$$\frac{\text{mirror image distance}}{\text{order distance} \times \text{wave-length}},$$

κ should be constant for all sharp lines on a given plate. This has been checked by measurements of sharp satellites from a water-cooled mercury lamp. A somewhat broad line of wave-length λ_b should have an order-separation $\kappa \times \lambda_b \times M_b$, where M_b is the distance between its mirror images, which will be sharp. The actual separation between its orders will be less than this amount, and the difference between the two values will be twice the amount by which each line is apparently displaced. If this correction is made in the reading of the higher-order fringe, the fractional part obtained will be independent of the intensity-distribution of the echelon.

If a line is in single-order position no such displacement will occur, and in an intermediate position the two displacements should very nearly cancel. This can be seen by drawing an envelope curve $y = \sin \alpha/\alpha$ and setting up ordinates α at intervals π. Thus the provision of means for varying the pressure is almost superfluous. The echelon chamber can be kept permanently evacuated so that the constant κ remains unaltered.

The importance of the reflection echelon as an instrument both for standard wave-length measurements and for hyperfine-structure work lies in the fact that the resolving-power of a Fabry-Perot interferometer is in practice limited by reflecting power of the films. While in theory the power can be increased by increasing the separation of the plates, in practice this is often not practicable beyond a certain point owing to the consequent overlapping of components. There is little doubt that with the development of optical technique, reflection echelons of a hundred or more plates will become practical possibilities in the not too distant future. The patterns then observed will show the true intensity-distribution of the spectral line.

A Fabry-Perot etalon with fairly dense, freshly made silver films should give for red light approximately the same resolving-power as a 25-plate echelon having the same plate-thickness as the gap of the interferometer. This comparison has been made several times, and one is forced to the conclusion that the actual resolving-power of the echelon is approximately twice as great. The discrepancy could easily arise if the etalon films were not strictly plane and parallel, and therefore special care was taken to ensure that no detectable error should occur. The only explanation that can be tentatively offered is that the inevitable minute errors in the Fabry-Perot instrument are multiplied, so that the multiple reflections occurring after a total error of $\frac{1}{4}\lambda$ has been reached tend to reduce instead of increasing the sharpness of the fringes. The reflection echelon plates are individually made, so that the possibility of additive errors is eliminated.

§ 9. DETERMINATION OF THE LENGTH OF LENGTH STANDARDS BY MEANS OF THE REFLECTION ECHELON

Two methods have hitherto been available for the purpose of standardizing length units in terms of the wave-length of some standard line: (1) Michelson's method, which has recently been further developed by Kösters(8), who used a Twyman and Green interferometer; (2) Benoit's method, which has been improved upon by Sears and Barrell(16).

The source of error most difficult to eliminate is the spurious displacement of the fringes that would occur if the standard source were complex and unsymmetrical. The possibility of this error was realized by Michelson who showed that if a line was perfectly sharp on one side and slightly shaded on the other, the fringes in his interferometer would be displaced by as much as 0·12 of a fringe-width even when the path difference was so small that the clearness or visibility of the fringes was not very much impaired. This effect is clearly shown in figure 3 for the case of the green mercury radiation.

Because of multiple reflection, the second method gives a fringe which is a much truer picture of the intensity curve of the line itself than is that given by the first method, and the spurious displacement owing to any lack of symmetry should be much reduced. The comparative coincidence in the final results of the two methods on the metre determination would, apart from the possibility of other errors cancelling its effect, apparently indicate that the red cadmium source is symmetrical.

On the other hand Nagaoka(18), using a special field-free cadmium lamp, reports alternations in the visibility of the Fabry-Perot fringes as the separation of the plates is increased to 20 cm. Heydenburg(19), who has studied the Paschen-Back effect in hyperfine structure and the polarization of the resonance line, concludes that the separation of the odd isotope levels at 6^1P_1 is 0·0126 cm.$^{-1}$ with the stronger even isotopes in between, so that the complex line 6438 Å. should be symmetrical.

The error due to lack of symmetry will also be present in the method suggested below, but its magnitude can be shown to vary inversely as the effective number of reflections employed. A densely silvered Fabry-Perot interferometer should give an effective number of about 25, but since it has to be used in series with stepping-up etalons in the normal Benoit method such heavy silvering cannot be employed.

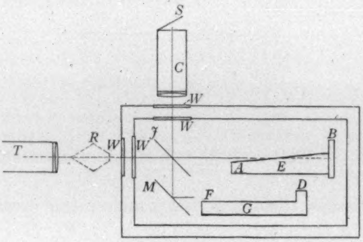


Figure 10.

Apart from any errors due to the multiplying or stepping-up process or errors in the determination of the phase-changes involved, there is the possibility of a change in the effective retardation of the primary etalon by the time it is being used in the stepping-up process. The principal advantage of Benoit's method, apart from the phase-displacement effect discussed above, lies in the very much reduced time taken to complete an observation, so that pressure and temperature conditions are fairly constant.

The method suggested below enables the determination of a length to be carried out in two operations which can be alternately checked in a few minutes. No corrections need be applied for phase-changes, and the limiting factor in accuracy seems to depend on the limits within which the temperature of the steel gauge can be determined. Finally, the adjustments required are so simple that the determination can be carried out in vacuo, and the complications of standardization in air can thus be avoided.

A silica reflection echelon of a total length equal to that of the distance to be standardized is made. If, for example, a metre gauge is desired, the plate-thickness may be 4·0000 cm. so that with a 25-plate instrument the distance between the ends will be a metre, within a few wave-lengths. The first plate is uncovered, and an extra large plane surface forms the last plate. This is now placed in one arm of a

Twyman and Green interferometer as shown in figure 10. For this purpose the cross slit S on the collimator C is closed, forming the required point source. The light transmitted by the half-silvered mirror J is reflected at M to the gauge G. When the surfaces of A and F, as well as B and D, are equidistant from J, the appearance of the field of view when the eye is placed at the focal plane of the objective of T will be as shown in figure 11 (A). If the distance between the planes A and B is exactly equal to that between the planes of F and D, the straight-line fringes of P and R, which come from B and D of figure 10, will be in alignment with the fringes in Q, which are due to F and A of figure 10. Without this equality there will be a displacement of the fringes which could be determined most conveniently by measuring the tilt of either of two equal parallel plates, one placed in each interferometer arm. If desired the echelon gap E, figure 11 (A), of the interferometer image can be eliminated by adding a suitable reversing prism R, figure 10.

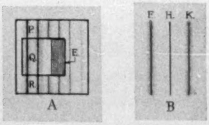


Figure 11.

The cross slit S is now tilted back and a micrometer eyepiece is added to the telescope T so that the appearance is as in figure 11 (B). H is the mirror image of the slit reflected from the open surfaces A or B. If the lines F and K are respectively the mth and $(m+1)$th orders for this wave-length, the exact order of interference at normal incidence is $(m + FH/FK)$. The integer of m is determined as in the previous section, so that with a total of N plates $(m+f)\lambda = 2AB/N$. Thus $(m+f)\lambda$ is the *mean* retardation due to a plate.

If the apparatus is enclosed in a double-walled box with suitable windows W the whole can be evacuated, and the tilting of the plate for equality of paths for E and G can be obtained by suitably geared remote control synchronous motors.

In this method one is not limited as to the choice of wave-lengths, since the resolving-power is not dependent on the reflecting-power. It might also be mentioned that the Twyman and Green or echelon fringes are entirely different from the fringes that have hitherto been used, and the echelon could be further used for the intercomparison of spectral lines throughout the spectrum to a degree of accuracy that has not yet been attained. The recent developments in the production of field-free sources seem to warrant the highest resolving-power.

§ 10. ACKNOWLEDGMENTS

I primarily wish to thank Prof. Takamine for his early encouragement and help, without which the first instrument could not have been constructed. I am indebted to Mr Rymer, B.A., of King's College for permission to include a set of his measure-

ments. Finally I wish to acknowledge the help of Mr Twyman, Mr Green and the technical staff of Messrs A. Hilger, Ltd., in connexion with the numerous difficulties that have had to be overcome.

REFERENCES

(1) A. A. Michelson. *Astro. phys. J.* **8**, 37 (1898).
(2) F. Twyman. *Proc. Opt. Conv.* **1**, 50 (1905).
3) R. G. Parker and A. J. Dalladay. *Phil. Mag.* **33**, 276 (1917).
(4) E. S. Johonnott. *Phil. Mag.* **47**, 501 (1899).
(5) H. Stansfield. *Phil. Mag.* **8**, 383 (1912).
(6) N. A. Kent and L. B. Taylor. *Proc. Amer. Acad.* **57**, 1 (1922).
(7) W. E. Williams. *Z. f. Phys.* **53**, 542 (1929).
(8) W. Kösters. *Z. f. Feinmechanik,* **34**, 55 (1926).
(9) F. Koláček. *Ann. d. Phys.* **39**, 1431 (1912).
(10) T. R. Merton. *Proc. R.S.* **113**, 704 (1926).
(11) A. Perard. *Compt. Rend.* **194**, 1633 (1932).
(12) W. E. Williams. British Patent Specification, No. 312, 534.
(13) R. Ritschl. *Z. f. Phys.* **79**, 1 (1932).
(14) J. W. Perry. *Journ. Sci. Insts.* **4**, 116 (1932).
(15) W. E. Williams. *Nature.* May 30th, 1931.
(16) J. E. Sears and H. Barrell. *Phil. Trans.* **231**, 125 (1932).
(17) T. R. Merton and S. Barratt. *Phil. Trans.* **222**, 380 (1922).
(18) H. Nagaoka. *Sci. Pap. Inst. Phys. Chem. Res. Tokyo,* **10**, 263 (1929).
(19) N. P. Heydenburg. *Phys. Rev.* **43**, 640 (1933).

DISCUSSION

Mr C. V. Jackson. It is quite possible to use the reflection echelon for the determination of relative wave-lengths but it is not nearly so suitable for this purpose as the Fabry-Perot etalon, on account of the difficulty of getting sufficiently large dispersion. Indeed D. A. Jackson and myself considered the idea four years ago and came to the conclusion that the echelon could not be used for wave-length determinations of the highest accuracy for this reason.

When one is measuring the wave-lengths of sharp lines, it is easily possible to use an etalon 10 cm. thick, and if a projection lens of focal length 1 m. is used the dispersion is about 150 mm./Å.[*] at λ 5000. (The dispersion of course varies with the ring measured, but the above is about the dispersion one gets with the rings usually used for wave-length determinations.)

Now with a 25-plate echelon with plates $7\frac{1}{2}$ mm. thick and with a step of 1 mm., the dispersion in the same region is only about 5 mm./Å. with a 1·7-metre objective or 8 mm./Å. with a 3-metre objective.

Thus, to get the same dispersion as that obtained with a 10-cm. etalon and a 1-metre objective, it would be necessary to use a reflection echelon about 4 m. long, with an objective of focal length 3 m. It would not be feasible to use a greater focal length, as this would make the relative aperture too low.

---

[*] This scale is necessary to obtain the highest accuracy attainable, since an error of 0·003 mm. (the minimum distance which can be reliably measured on a photographic plate) would give an error of 1 in 2×10^8 in the wave-length.

The determination of the phase correction of etalon plates presents no difficulty whatever. Indeed the data for its calculation are immediately at hand in the plates one takes, with different interferometer gaps, for measuring the wave-lengths.

It is quite true that the fringes obtained with an echelon have a smaller instrumental width than those obtained with an etalon, but this has no bearing on the accuracy obtainable in wave-length determinations, because one can always use an interference path sufficiently great to render the instrumental width small in comparison with the width of the line itself.

Although I have come to the conclusion, for the reasons given above, that the reflecting echelon is definitely unsuitable for the most accurate wave-length determinations, I do not wish to belittle an instrument for which I have a very great admiration. It is hardly overstating the case to say that as a high-resolving-power instrument for investigating hyperfine structure, it is far superior to any other instrument now known.

With regard to the silvering of interferometer plates, I think it necessary to point out that Dr Sears's etalon could not have been improved in any way. With the long interference path used by Dr Sears the reflecting-power of his silver was already high enough to give an instrumental width far narrower than the width of the Cd red line, or any other line known. The effect of heavier silvering would merely be to reduce the intensity of the rings. This is obviously disadvantageous.

Mr J. E. SEARS, Junr. The author's work on the reflection echelon has provided a powerful instrument of a new type which, I feel sure, will lead to interesting results.

It may be of interest to mention that we have only last week completed, at the National Physical Laboratory, a full redetermination of the length of the metre in terms of the cadmium red radiation, both in air free from CO_2 and in vacuo. The resulting wave-length in vacuo for λ_R is $0{\cdot}64402502\,\mu$., with a probable error so far as concerns the optical side of the measurements of less than 2 parts in 10^8. I mention this because the result is appreciably different from the figure quoted by Mr Williams, namely, $0{\cdot}64402513\,\mu$., taken from our preliminary measurements. The discrepancy is accounted for almost entirely by the fact that in the interval between the preliminary and final measurements the British national copy of the metre, No. 16, was re-verified at Sèvres, and its assigned value was reduced by $0{\cdot}19$ parts in 10^6.

The author mentions in his paper the possibility that the red line of cadmium has some fine structure, and I believe he has obtained definite evidence of this with the aid of his reflection echelon; I hope he will give us more information as to this as soon as he is in a position to do so. In the meantime, however, it may allay some doubts to record that in view of this possibility we carried out our work on the measurement of the metre starting with two independent basic etalons of length approximately $\frac{1}{12}$ m. and $\frac{1}{5}$ m. respectively, and found no measurable difference between the results.

The author mentions that owing to the necessity of using Brewster fringes for stepping up in the Benoit-Fabry-Perot procedure the plates of the primary etalon must be silvered fairly lightly, and he suggests that they will therefore not give as many as 25 reflections. Actually the plates used by us, which now appear somewhat tarnished after two months' continuous use, still give 18 visible reflections of a light-source such as the filament of an incandescent lamp. When new they probably gave between 20 and 25 reflections.

I am particularly interested in the author's suggestion that a reflection echelon should be used as a standard of length. It is a most attractive idea and has evident advantages, though it would be somewhat costly. From the metrological standpoint, however, there is one disadvantage that should be mentioned, namely that the gauge bar with a heel, with its two measuring surfaces facing the same way and not on the same axis, is obviously inconvenient. Some means might, however, be found to overcome this objection.

AUTHOR's reply. In reply to Mr C. V. Jackson: I had understood that Mr D. A. Jackson had tried to use the reflection echelon as a means of measuring wave-lengths. The real reason of the apparent failure of the method is to be found not in any lack of dispersion but in the fact that with the Littrow type of mounting which he has adopted, the simple equation (2) does not apply and the more complicated equation (3) of § 7 has to be taken. This would necessitate measurements being made in two coordinates.

If spectral lines were simple and symmetrical a Michelson interferometer would suffice for the most accurate wave-length measurements, since the path-difference could be increased as required. Unfortunately very few if any such homogeneous lines exist, and it would only be in very rare instances that a Fabry-Perot etalon with a gap of 10 cm. could be used. This is shown from Mr C. V. Jackson's own work* on the wave-lengths of the Krypton lines which have been considered by various foreign metrologists to be extremely sharp. The largest gap he used was 3 cm., although a gap of 10 cm. was attainable with the instrument. In spite of its lower dispersion a 35-plate echelon of plate-thickness 7·3 mm. clearly shows fine structure in lines that the much-larger-gap etalon apparently fails to resolve. Surely if the dispersion suffices to show the components clearly separated it can be used with correspondingly increased accuracy to measure their individual wave-lengths. It is not the linear dispersion of an instrument that finally sets the limit to the accuracy of the wave-length measurement, but its resolving-power, provided this has not been attained at the expense of overlapping orders. All that is needed as regards dispersion is that it should be sufficient to eliminate any effects due to the grain of the plate. Many spectral lines (especially when emitted from a Paschen-Schuler hollow-cathode discharge) are so intense that a suitable achromatic lens could be placed in front of s_2, figure 7, to give a five-fold magnification of the pattern on the slit of the spectrograph. Although the dispersion would then be increased, the lines themselves would be correspondingly wider and the real gain in accuracy would be small.

---

* *Proc. R. S.* **138**, 147 (1932).

With the etalon method one has to measure the diameters of comparatively large rings of diameter about 1·5 cm., and the slightest shrinkage of the photographic film will appreciably alter the apparent order at the centre. In the new method, the sharp reference line need only be a fraction of an order away from the interference fringe, so that the shrinkage effect would be negligible. The measurements carried out so far with reflection echelons of thickness 7 mm. indicate that if correspondingly sharp lines are obtained with a 25-plate instrument of plate-thickness 4 cm. (the construction of which is a practical possibility) an accuracy of 1 part in 10^8 would be attainable at a wave-length of 6000 Å.

I am much obliged to Mr Sears for his kind interest and am indebted to him for a wave-length standard with which to make intercomparisons. He mentions that his etalons gave about 25 multiple reflections. If we assume that the weakest image has an intensity 0·01 or 0·001 of the first, the approximate reflection coefficient of the films can be obtained, since $R^{25} = 0{\cdot}01$ or $0{\cdot}001$ as the case may be. The calculated values of the coefficients are 0·759 and 0·832 respectively. An inspection of Hansen's curve A given on p. 99 of my little booklet* shows that the corresponding effective numbers of reflections are approximately 11 and 16. That is to say, the etalon should be equivalent to an 11- or 16-plate reflection echelon of the same thickness. The real advantage of the reflection echelon is this: above a certain point high revolving-power with the Fabry-Perot interferometer can only be obtained by increasing the plate-separation, which increases the probability of overlapping of orders of satellites. In the reflection echelon high resolving-power is attained by simply adding extra plates.

---

* *Applications of Interferometry* (Methuen).

629.1.038:534.41

OBSERVATIONS ON THE INTENSITY OF LOW-FREQUENCY SOUNDS CLOSE TO A METAL AIRSCREW

By C. F. B. KEMP, A.R.C.S., B.Sc., D.I.C.

Received March 3, 1933. *Read June* 2, 1933.

ABSTRACT. A condenser transmitter and continuously recording cathode-ray tube have been used to obtain the wave-form of the sound from a metal airscrew operating at zero rate of advance. Fourier analysis has been applied to records taken at various distances up to 300 ft. from the airscrew and the rate of decay of intensity has been determined for the first three harmonics. At distances greater than 100 ft. the inverse-square law of distance has been found to hold, but at nearer points the rate of decay is not constant and varies in a complicated manner. The average rate of decay is less than that given by the inverse-square law, a result not in concordance with recent determinations by Obata, Yosida and Morita. An explanation of this difference is given.

1. INTRODUCTION

An interesting property of the sound generated by a complex source, such as a revolving airscrew, is the rate of decay of intensity of the low-frequency components at distances which are not great compared with the dimensions of the source or with the various wave-lengths. If the sound from the airscrew can be isolated from the sound emanating from the power plant, a convenient method of obtaining this information is to apply Fourier analysis to wave-form records of pressure-amplitude. The results so derived may be of value for the purpose of testing proposed theories concerning the airscrew as a source of sound. The wave-forms themselves are of considerable interest, inasmuch as they provide material for comparing the physical magnitudes of the high-pitched sounds, which are so noticeable in the neighbourhood of an airscrew, with those of the low-pitched sounds which, on occasion, are felt rather than heard. Furthermore, Eisner, Rehm and Schuchmann(1) have pointed out that the search-tone methods of frequency-analysis sometimes employed in the analysis of aeroplane noise give inaccurate results for components having frequencies of less than 100 ~, and that more detailed knowledge of the intensity of these components is required, especially close to the aeroplane. It is hoped that the results given in this paper may assist in the collection of this information so far as the airscrew sound is concerned.

2. EQUIPMENT AND SCOPE OF EXPERIMENT

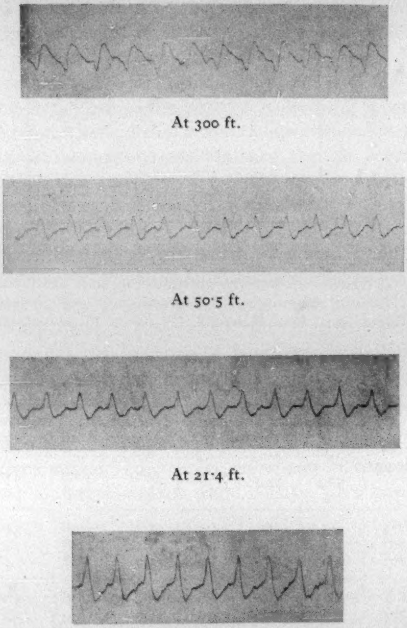
The airscrew used was of the Leitner-Watts type with hollow steel blades; it had a diameter of 11·5 ft. and a pitch setting of − 5 degrees against the centre scale. The power plant was a Napier-Lion engine installed in a tethered wingless fuselage (D.H. 9A type), which was adjusted in height so that the plane of rotation of the airscrew was vertical, the tips of the blades clearing the ground by 2 ft. As in previous experiments conducted by the author(2), this equipment was set up remote from buildings, in order to avoid errors due to the reflection of sound therefrom. The sound from the engine exhaust was effectively silenced by attaching to the cylinder stub pipes lagged manifolds terminating in a silencing pit.

The sound from the airscrew was received by a calibrated condenser transmitter (G.E.C. pattern) placed with the diaphragm almost flush with the ground. In this way, the interference effect of the waves reflected once from the ground between the airscrew and the transmitter was minimized. The sound-currents were amplified once and passed over a low impedance line to the laboratory, where, after further controlled amplification, they actuated a Von Ardenne cathode-ray-tube, the wave-form being recorded on a strip of sensitized paper moving at uniform speed.

Observations were made in the plane of rotation at the following horizontal distances (in feet) from the airscrew boss: 300, 100, 50, 40, 30, 20 and 10. The plane of rotation was chosen because earlier experiments had shown the sound-output to be particularly steady in this direction. To record the wave-form, the engine was first allowed to attain a speed of 1700 ± 10 r.p.m. A calibrated step-by-step amplification-control was then set so that the maximum excursion of the cathode-ray spot was such that the photographic record would have an amplitude adequate for purposes of analysis and inspection. The duration of each recording period was a few seconds.

3. RESULTS

Figure 1 comprises reproductions of typical wave-form records. By inspection, successive waves on any given record are sufficiently alike for Fourier analysis to be applied with accuracy in the computation of the lower-order harmonics. This repetition of wave form has an important bearing on the effectiveness of the exhaust-silencing. The fundamental frequency in the sound from the airscrew is clearly 37·3 ~ for an engine speed of 1700 r.p.m. The Lion engine has a reduction gear of 1 to 0·659, so that the fundamental frequency of the exhaust sound is 56·7 ~. With few exceptions the frequencies comprising the two trains of harmonics are, in effect, incommensurable, and hence repetition of wave-form could not occur if the exhaust sound were present in any appreciable quantity. The period of repetition of the waves is the period of the fundamental blade-frequency. The method of silencing can therefore be regarded as adequate. Inspection also shows the maximum amplitude of any wave-trace to be very steady, and not only was this steadiness evident throughout the length of each record, but the amplitude of the cathode-ray spot-displacement was remarkably constant over long periods when the engine had attained constant speed. This may be characteristic of metal airscrews, for both two-bladed and four-bladed wooden airscrews, when driven by the same engine under similar weather conditions, produced amplitudes and wave-forms of very appreciably less constant nature.



At 300 ft.

At 50·5 ft.

At 21·4 ft.

At 12·6 ft.

Figure 1. Specimen oscillograms of airscrew sound.

Figure 2 incorporates the results of Fourier analysis after correction for the overall frequency characteristic of the recording apparatus. This characteristic was sensibly flat from 55 ~ upwards, the presence of two line transformers accounting for some attenuation at lower frequencies. For the purpose of analysis, the ordinates of six successive waves were measured on each record. These were averaged to give a mean wave-form which was then analysed. In this way, small variations in wave-form were smoothed and the effect of any residual frequencies, not exact multiples of the fundamental blade frequency, was minimized by interference. The two sets of results given in the figure were obtained on different days and correspond to engine-speeds of 1700 r.p.m. and 1750 r.p.m. The values of the pressure-amplitude also are tabulated.

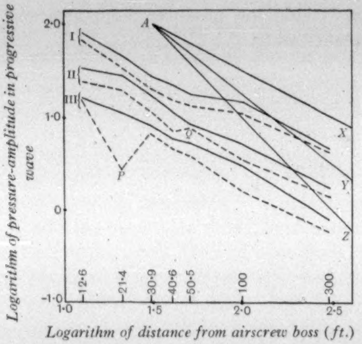


Figure 2. Experimental relationship between pressure-amplitude and distance from the centre of the airscrew. Laws of intensity: *AX* inverse-square, *AY* inverse-cube, *AZ* inverse-fourth-power. Harmonics: I first, II second, III third. Engine-speeds: 1750 r.p.m. ——, 1700 r.p.m. - - - - -.

Table 1.

Engine-speed (r.p.m.)	Frequency	Pressure-amplitude (dyne/cm.^{2}) in progressive wave at the following distances from the boss (ft.)						
		300	100	50·5 (50)	40·6 (40)	30·9 (30)	21·4 (20)	12·6 (10)
1700	37·3	4·3	11·2	13·3	15·4	20·6	34·6	68·4
	74·6	1·4	3·5	7·7	7·1	11·6	19·7	24·8
	111·9	0·6	1·6	3·9	4·7	6·8	2·8	15·8
1750	38·8	4·7	14·9	17·6	22·4	27·8	46·0	81·6
	77·6	1·8	5·3	8·6	11·7	18·0	28·2	34·4
	116·4	0·8	3·1	5·3	6·0	8·3	11·1	16·0

The figures in brackets are horizontal distances from the airscrew boss.

The two sets of results are in agreement so far as the general form of the unsmoothed curves is concerned. No significance is attached to the departure of the two plotted points *P* and *Q* from the general trend of results, such occasional discrepancies being inseparable from experiments carried out in the open air. At distances greater than 100 ft. the intensity falls off according to the inverse-square law of distance, as might be expected, since distances of this order are large compared with the dimensions of the source and with the wave-length. The greater rate of decay indicated for the third harmonic (at 1750 r.p.m.) is probably erroneous and due to a slight over-estimation of the pressure-amplitude at 100 ft., the logarithmic scale causing a relatively large change in the position of the plotted point. At nearer distances are found various rates of decay for which no reason can be advanced at present. Thus, the fundamental component (first harmonic) has an abnormally slow rate of decay between 50 ft. and 100 ft., but at lesser distances both the inverse-square and inverse-cube laws of distance are followed. It should be noted that the abscissae in figure 2 are the distances of the microphone from the airscrew boss. Had the horizontal distances from the boss been plotted, the inverse-square law alone would have applied approximately between 10 ft. and 50 ft., as may be seen by reference to the pressure-amplitude values given in the table. According to both sets of results the second harmonic follows the inverse-cube law between 21·4 ft. and about 40 ft., but very close to the airscrew it decays at a lesser rate than the inverse-square. Further, a comparison of the results obtained at 300 ft. with those obtained at the nearest microphone-position show that the average rate of decay of intensity is less than that corresponding to the inverse-square law of distance, whether the distance is measured from the airscrew boss or from a point on the ground vertically beneath the boss.

These observations are apparently at variance with those recently put forward by Obata, Yosida and Morita(3). Experiments in which an audiometer was used showed that the loudness of the sound from an airscrew varies inversely as the distance, within the limits of experimental error, and it was stated that this corresponds to a rate of decay of intensity much in excess of the inverse-square law of distance. In an obvious notation, this result may be put in the form

$$db = -m\,(d_2 - d_1)$$ db, m, d_1, d_2

where m is in decibels per unit distance.

Assuming that the loudness of a complex sound may be converted into terms of physical intensity by the expression known to hold for pure tones, then if $I \propto d^{-n}$ it follows that I, n

$$n = \frac{m}{10}\,\frac{d_2 - d_1}{\log d_2 - \log d_1}.$$

For distances between 30 and 100 metres $m = 0{\cdot}224$, giving $n = 3$, in correspondence with the inverse-cube law. Apart however from the above assumption, which is open to serious dispute, it must be remembered that a doubling and a halving of the physical intensity both produce a change in loudness of only 3*db* and that errors of this order are common in audiometer determinations, especially those made in the open. It does not seem possible, therefore, that adequate deductions concerning the rate of decay of intensity can be made from observations of a physiological character.

The specimen records shown in figure 1 indicate that no very marked change in wave-form occurs as the airscrew is approached. At first sight the wave-form at 300 ft. appears different from the others, but actually it is merely a reversed and inverted version, due to an inadvertent crossing of the leads between the line transformers. The wave-form at 300 ft. is smooth, but superimposed wavelets of comparatively high frequency become increasingly noticeable as the distance is diminished. Even at the nearest point to the airscrew, the average pressure-amplitude of these disturbances is only about 4 per cent of the maximum, an interesting fact in view of the impression made on the ear at such a close range.

4. ACKNOWLEDGMENTS

This experiment, which was carried out in connexion with the work of the Aircraft Noise Sub-Committe of the Aeronautical Research Committee, was initiated by Dr W. S. Tucker, D.Sc., O.B.E. The airscrew equipment was supplied for this and similar experiments by the Director of Scientific Research, Air Ministry.

REFERENCES

(1) Eisner, F., Rehm, H. and Schuchmann, H. *Elektrische Nachrichten-Technik*, **9**, 323–33 (1932).
(2) Kemp, C. F. B. *Proc. Phys. Soc.* **44**, 151–65 (1932).
(3) Obata, J., Yosida, Y. and Morita, S. *Aero. Research Inst., Tokyo Imperial University, Report No.* 79 (1932).

DISCUSSION

Mr J. Guild. In order to appreciate the physical significance of the author's results it would be necessary to have information which, while it may be quite well known to aeronautical experts, is not given in the paper. One point of importance is: how is the sound produced? Are we here concerned with a pure siren action due to the alternate arrest and release of portions of the air flowing through the plane of the screw (that is, can we regard the screw itself as a perfectly rigid body with no movement other than that of rotation?), or does the sound arise mainly or in any appreciable proportion from pulsations set up in the blades, which then act as vibrating bars? If the latter cause is responsible, what are the modes of vibration? Without an answer to these questions we cannot get at the phase and intensity relations which determine the form of the wave-front in the immediate neighbourhood of the source.

It is also necessary that we should know the distribution of air-velocity along the path followed by the waves; but no mention of air-velocities, which must be considerable in the vicinity of an aeroplane propeller, occurs in the paper.

The inclusion in technical papers of the information necessary to enable the results to be related to the physical conditions of the problem, though it would not add to the technical value of the results, would greatly increase their scientific value as additions to the general body of knowledge.

Dr A. B. Wood enquired whether the author found any interference between sounds reaching the detector directly and by reflection from the ground. In connexion with § 1 he pointed out that the intensity of a sound depends on pitch as well as amplitude.

Author's reply. In reply to Mr Guild: (1) The low-frequency sound here considered arises from the periodic impact of the airscrew blades upon the air in the path of rotation*. (2) Although elastic vibrations of the blades are present†, they constitute only a minor source of sound. (3) Variations in air-velocity may be disregarded, since the measurements were made in the plane of rotation, outside the slipstream (see § 2). (4) Existing knowledge of the sound generated by airscrews was discussed in a previous paper by the author‡ and a list of references was then given.

In reply to Dr A. B. Wood: (1) As was stated in § 2, the diaphragm of the microphone was almost flush with the ground. The recorded wave-form was therefore that of the directly received sound alone. (2) The intensity is given by $I = p^2/r$ where p is the r.m.s. value of the pressure-variation and r the radiation resistance of the medium. The quantity measured in the experiments was p, hence pitch does not enter into the calculations.

---

* E. J. Lynam and H. A. Webb, *Aero. Research Committee R. and M., No.* 624 (1919); M. D. Hart, *Aero. Research Committee R. and M., No.* 1310 (1930).

† A. Fage, *Proc. R. S.* A., **107**, 456–68 (1925).

‡ C. F. B. Kemp, *Proc. Phys. Soc.* **44**, 151–65 (1932).

535·337 : 546.295

PRESSURE EFFECTS IN THE SPECTRA Xe I AND Xe II

By J. F. HEARD, Ph.D., 1851 Exhibition Scholar,
Imperial College, London

Communicated by Prof. A. Fowler, F.R.S., May 30, 1933.
Read July 7, 1933.

ABSTRACT. The first and second spectra of xenon have been examined for pressure effects. At high pressure, lines of the Xe I spectrum show broadenings which correspond qualitatively to their respective Stark effects. This points to the existence of strong interionic electric fields within the discharge. Many pressure displacements in the Xe II spectrum are also found, and it is suggested that these too have their origin in interionic fields.

§ 1. INTRODUCTION

Numerous investigations of the broadening and displacement of spectral lines when excited under conditions of high current-densities and high vapour-pressures have been made. In the main these investigations have supported the view that such broadenings and displacements are, to some extent at least, a result of interionic electric fields. In arc spectra it has often been possible to correlate qualitatively the broadening and displacement with the known Stark effects. Thus, for example, Merton and Nicholson* have shown that the symmetrical broadening of the Balmer lines in a condensed discharge is that to be expected as a result of inhomogeneous electric fields; and Merton† and Takamine‡ have demonstrated a corresponding effect for helium lines excited by a condensed discharge or in gas at high pressure. So-called pressure shifts are also known in the second spectra of many elements. Pretty§ has made systematic investigations of these shifts in the spectra of ionized nitrogen, oxygen, neon and argon, and found reasons to believe that they arose from electric fields, although actual Stark effect data were not available for comparison.

In the xenon arc spectrum Humphreys|| reported that he was unable to discover any shift of the lines with varying pressure of the gas, but that under condensed discharge conditions he observed some asymmetric broadenings toward the red. These he attributed to the effect of electric fields. Because Stark displacements are now known¶ to be unusually large and abundant in the xenon arc spectrum, it was of interest to the writer to investigate the effects of pressures higher than

---

* *Phil. Trans.* **216** A, 459 (1917).

† *Proc. R.S.* A. **95**, 30 (1918).

‡ *Sci. Papers of Inst. of Phys. and Chem. Research* (Tokio), No. 69, 55 (1926).

§ *Proc. Phys. Soc.* **41**, 442 (1929); **43**, 279 (1931).

|| *Bureau of Standards J. of Research*, **5**, 1041 (1931).

¶ H. W. Harkness and J. F. Heard, *Proc. R. S.* A, **139**, 416 (1933).

those used by Humphreys. The results show that broadened lines are emitted by an uncondensed discharge in the gas at pressures of several centimetres of mercury and that these broadenings are to be attributed to the effect of interionic electric fields. The pressure effects in the first spark spectrum were also investigated and numerous shifts are reported and discussed.

§ 2. EXPERIMENTAL

The sources of light were pyrex discharge tubes of the Geissler type which could be viewed end on. They were fitted with aluminium and magnesium electrodes, the magnesium serving to clean up impurities. Into one such discharge tube xenon was admitted to a pressure of about 4 mm. and into another to a pressure of about 4 cm., the latter pressure having been found to be the most suitable for a high-pressure source.

A 12-in. induction coil and a 40-kV. transformer were used as means of excitation. When a condensed discharge was required a 0·07-μF. condenser and a 2 mm. spark gap were included in the circuit.

The light was examined by means of a Hilger E1 quartz spectrograph and a 10-ft. concave diffraction grating in an Eagle mounting.

§ 3. BROADENED LINES IN THE Xe I SPECTRUM

The spectrum of the condensed discharge in the low-pressure source showed the asymmetric broadenings mentioned by Humphreys*. It was discovered, moreover, that similar broadened lines could be produced by an uncondensed discharge in the 4-cm. source. In this case the transformer was used. The potential drop across the tube was about 15,000 V. and the current was about 25 mA. Under such conditions the discharge was disruptive and, in addition to the Xe I spectrum, the Xe II spectrum was excited though not strongly.

To say that the lines were broadened is, perhaps, less accurate than to say that certain lines were accompanied by wings on one side or both sides. A comparison of these with the known Stark displacements of the lines has shown conclusively that the wings arise from heterogeneous fields within the discharge. Thus, lines such as λ 6498·71, λ 5894·99, λ 5875·02, which have Stark displacements toward the blue only, have wings on the blue side but are perfectly sharp on the red side; lines such as λ 6198·25 and λ 6179·66, which have Stark displacements toward the red only, are diffuse on the red and sharp on the blue side; while lines which have Stark displacements on both sides show a distribution of intensity corresponding to the displacements and intensities of the Stark components. λ 6318·08 ($2p_8$–$6d'_4$) is an example of the latter type. The correspondence between its pressure broadening and its Stark effect is demonstrated in (*a*), (*b*) and (*c*) of the accompanying plate. A calculation indicates that some of the transitions responsible for the wings of this line must have taken place in the presence of electric fields certainly greater than 100,000 V./cm. Since the terminal potential of the tube was only 15,000 V., and since none of the observed light came from the neighbourhood of the electrodes, it must be assumed that the electric fields were of an interionic nature.

---

* *Loc. cit.*

Note. The following observation, although divorced from the present subject of discussion, is probably worth reporting here. When the high-pressure xenon discharge tube was excited by a weak discharge the greater part of the visible light consisted of the Swan band system of C_2. The appearance of these bands was very similar to the appearance of the Swan bands excited by Johnson*, using high-pressure argon. The mechanism is, no doubt, of a similar nature, for in the present case the discharge tubes contained traces of carbon and hydrogen as in Johnson's experiments.

§4. BROADENED AND DISPLACED LINES IN THE Xe II SPECTRUM

The first spark spectrum of xenon as excited by a condensed discharge in the tube at 4 cm. has been compared with that excited in a similar way in the low-pressure tube. A 0·07-μF. condenser was shunted across an induction coil and a 2-mm. spark gap was placed in series with the tube. The spectral region investigated was that between λ 3500 and λ 7000.

All the Xe II lines excited in the high-pressure source are quite diffuse, and associated with the spectrum is a continuous background which makes it impossible to observe lines having less than a certain intensity. Of the lines observed many show displacements of their centres of gravity. Most of the displacements, including all the larger ones, are toward the red. The breadth of a line increases with the magnitude of its displacement, and consequently it is difficult to measure the displacements with precision; but an attempt has been made to estimate as well as possible the displacements of the centres of gravity. In the plate there is reproduced a portion of the spectrum showing some typical displacements of Xe II lines.

A partial analysis of the Xe II spectrum has been published by Humphreys, de Bruin and Meggers†. Many of their identified lines have been observed in the high-pressure spectrum. Table 1 lists these with the classification of the above authors and with the shifts observed in the present investigation.

From the observations in table 1 it has been possible to assign displacements to the energy levels involved in the various transitions. In general, each level is involved in several of the observed lines. The agreement is, naturally, not perfect, but it is within about 0·2 cm^{-1}. For this reason the small displacements have been recorded only as multiples of 0·3 cm^{-1}.

The displacements of the lines reveal not the absolute displacements of the levels involved but merely their relative displacements. In recording the displacements in table 2, the writer has chosen that arrangement which assigns zero displacement to the greatest number of levels.

---

* *Phil. Trans.* **226**, 157 (1927).

† *Bureau of Standards J. of Research*, **6**, 287 (1931).

Table 1. Identified lines in the Xe II spectrum with their pressure displacements

Wave-length*	Classification	Displacement (cm.⁻¹)	Wave-length*	Classification	Displacement (cm.⁻¹)
6790·34	$(6s)\,^2D_{1\frac{1}{2}}-(6p)\,^2D^0_{1\frac{1}{2}}$	− 0·5	5368·07	$(5d)\,X_{1\frac{1}{2}}-(6p)\,^2P^0_{\frac{1}{2}}$	0
6788·60	$(6s)\,^2D_{2\frac{1}{2}}-(6p)\,^2D^0_{1\frac{1}{2}}$	− 0·6	5313·89	$(6p)\,^4D^0_{3\frac{1}{2}}-(7s)\,^4P_{2\frac{1}{2}}$	− 5·2
6694·35	$(6s)\,^4P_{\frac{1}{2}}-(6p)\,^4S^0_{1\frac{1}{2}}$	− 0·4	5309·28	$(6s)\,^2P_{1\frac{1}{2}}-(6p)\,^2D^0_{1\frac{1}{2}}$	0
6598·80	$(6s)\,^2D_{1\frac{1}{2}}-(6p)\,^2D^0_{2\frac{1}{2}}$	− 0·6	5292·22	$(6s)\,^4P_{2\frac{1}{2}}-(6p)\,^4P_{2\frac{1}{2}}$	+ 0·4
6597·24	$(6s)\,^2D_{2\frac{1}{2}}-(6p)\,^2D^0_{2\frac{1}{2}}$	− 0·6	5260·44	$(5d)\,X_{1\frac{1}{2}}-(6p)\,^2P^0_{1\frac{1}{2}}$	0
6343·97	$(5d)\,^4D_{1\frac{1}{2}}-(6p)\,^4S^0_{1\frac{1}{2}}$	0	5191·38	$(5d)\,X_{1\frac{1}{2}}-(6p)\,^2S^0_{\frac{1}{2}}$	0
6277·54	$(5d)\,^4D_{1\frac{1}{2}}-(6p)\,^4P^0_{2\frac{1}{2}}$	0	5122·44	$(6p)\,^4P^0_{\frac{1}{2}}-(7s)\,^4P_{1\frac{1}{2}}$	− 6·2
6097·60	$(5d)\,^4D_{2\frac{1}{2}}-(6p)\,^4S^0_{1\frac{1}{2}}$	− 0·6	5080·66	$(6p)\,^4P^0_{1\frac{1}{2}}-(7s)\,^4P_{1\frac{1}{2}}$	− 5·1
6093·53	$(6p)\,^4D^0_{1\frac{1}{2}}-(7s)\,^4P_{1\frac{1}{2}}$	large (−)	4988·78	$(6s)\,^2P_{\frac{1}{2}}-(6p)\,^2P^0_{1\frac{1}{2}}$	− 1·2
6051·18	$(5d)\,^4D_{3\frac{1}{2}}-(6p)\,^4P^0_{2\frac{1}{2}}$	− 0·9	4919·68	$(5d)\,X_{1\frac{1}{2}}-(6p)\,^2P^0_{1\frac{1}{2}}$	0
6036·20	$(5d)\,^4D_{2\frac{1}{2}}-(6p)\,^4P^0_{2\frac{1}{2}}$	− 0·5	4890·10	$(6s)\,^4P_{2\frac{1}{2}}-(6p)\,^4P^0_{1\frac{1}{2}}$	0
5976·47	$(6s)\,^4P_{1\frac{1}{2}}-(6p)\,^4S^0_{1\frac{1}{2}}$	+ 0·5	4862·50	$(6p)\,^4P^0_{2\frac{1}{2}}-(7s)\,^4P_{2\frac{1}{2}}$	− 5·8
5945·54	$(6s)\,^4P_{\frac{1}{2}}-(6p)\,^4P^0_{\frac{1}{2}}$	− 0·3	4823·38	$(6p)\,^4S^0_{1\frac{1}{2}}-(7s)\,^4P_{2\frac{1}{2}}$	− 5·7
5917·45	$(6s)\,^4P_{1\frac{1}{2}}-(6p)\,^4P^0_{2\frac{1}{2}}$	0	4818·04	$(5d)\,^4D_{1\frac{1}{2}}-(6p)\,^4D^0_{1\frac{1}{2}}$	− 0·7
5776·40	$(5d)\,X_{\frac{1}{2}}-(6p)\,^2D^0_{1\frac{1}{2}}$	0	4779·18	$(sp^6)\,^2S_{\frac{1}{2}}-(6p)\,^4S^0_{1\frac{1}{2}}$	− 0·7
5751·05	$(6s)\,^2P_{\frac{1}{2}}-(6p)\,^2D^0_{1\frac{1}{2}}$	− 1·3	4674·55	$(5d)\,^4D_{2\frac{1}{2}}-(6p)\,^4D^0_{1\frac{1}{2}}$	− 0·5
5719·62	$(5d)\,^4D_{1\frac{1}{2}}-(6p)\,^4P^0_{1\frac{1}{2}}$	− 0·3	4653·00	$(6s)\,^2P_{1\frac{1}{2}}-(6p)\,^2P^0_{1\frac{1}{2}}$	0
5667·58	$(5d)\,^4D_{1\frac{1}{2}}-(6p)\,^4P^0_{\frac{1}{2}}$	− 0·5	4603·05	$(6s)\,^4P_{1\frac{1}{2}}-(6p)\,^4D^0_{1\frac{1}{2}}$	0
5659·40	$(5d)\,X_{1\frac{1}{2}}-(6p)\,^2D^0_{1\frac{1}{2}}$	0	4384·92	$(sp^6)\,^2S_{\frac{1}{2}}-(6p)\,^4P^0_{\frac{1}{2}}$	− 0·9
5572·21	$(5d)\,X_{\frac{1}{2}}-(6p)\,^2S^0_{\frac{1}{2}}$	0	4215·63	$(6s)\,^4P_{2\frac{1}{2}}-(6p)\,^4D^0_{1\frac{1}{2}}$	0
5472·62	$(5d)\,^4D_{3\frac{1}{2}}-(6p)\,^4D^0_{3\frac{1}{2}}$	− 0·9	4100·34	$(5d)\,^4D_{1\frac{1}{2}}-(6p)\,^4D^0_{\frac{1}{2}}$	0
5460·40	$(5d)\,^4D_{2\frac{1}{2}}-(6p)\,^4D^0_{3\frac{1}{2}}$	− 0·9	3905·89	$(5d)\,^4D_{1\frac{1}{2}}-(6p)\,^2D^0_{1\frac{1}{2}}$	0
5450·49	$(6s)\,^2P_{\frac{1}{2}}-(6p)\,^2P^0_{\frac{1}{2}}$	− 1·3	3858·53	$(sp^6)\,^2S_{\frac{1}{2}}-(6p)\,^4D^0_{1\frac{1}{2}}$	− 1·0
5438·98	$(6p)\,^4D^0_{1\frac{1}{2}}-(7s)\,^4P_{\frac{1}{2}}$	0	3848·60	$(5d)\,^4D_{\frac{1}{2}}-(6p)\,^2D^0_{1\frac{1}{2}}$	0
5419·17	$(6s)\,^4P_{1\frac{1}{2}}-(6p)\,^4P^0_{1\frac{1}{2}}$	0	3811·06	$(5d)\,^4D_{2\frac{1}{2}}-(6p)\,^2D^0_{1\frac{1}{2}}$	− 0·7
5372·41	$(6s)\,^4P_{1\frac{1}{2}}-(6p)\,^4P^0_{\frac{1}{2}}$	0	3500·37	$(6s)\,^4P_{2\frac{1}{2}}-(6p)\,^2D^0_{1\frac{1}{2}}$	0

* The wave-lengths are those given by Humphreys, de Bruin and Meggers and are the wave-lengths in vacuo.

It will be observed that the only large displacements in table 2 are associated with two of the 7*s* levels. This fact is in agreement with the results of Pretty* on the corresponding A II and Ne II spectra, where the larger displacements are associated with terms of higher principal quantum numbers. In Pretty's results, however, members of a multiplet always give rise to displacements which are equal within the possible errors of measurement, whereas in the Xe II spectrum this is not the case. The most notable exception to such a rule lies in the smallness of the displacement of the term $(s^2p^4.7s)\,{}^4P_{\frac{1}{2}}$, as compared with the displacements of the other two members of the multiplet.

---

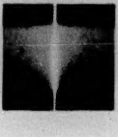
* *Loc. cit.*

Table 2. Pressure displacements of the known energy levels of Xe II

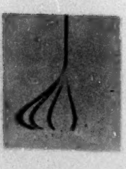
Notation	Term value	Displacement (cm.⁻¹)	Notation	Term value	Displacement (cm.⁻¹)
$(sp^6)\ {}^2S_{\frac{1}{2}}$	80,195	− 0·6	${}^4P^0_{2\frac{1}{2}}$	59,110	0
$(s^2p^4.6s)\ {}^4P_{2\frac{1}{2}}$	78,000	+ 0·3	${}^4P^0_{1\frac{1}{2}}$	57,556	+ 0·3
${}^4P_{1\frac{1}{2}}$	76,004	+ 0·3	${}^4P^0_{\frac{1}{2}}$	57,396	+ 0·3
${}^4P_{\frac{1}{2}}$	74,210	0	${}^4D^0_{3\frac{1}{2}}$	57,363	+ 0·3
$(s^2p^4.5d)\ {}^4D_{3\frac{1}{2}}$	75,631	− 0·6	${}^4D^0_{1\frac{1}{2}}$	54,286	+ 0·3
${}^4D_{2\frac{1}{2}}$	75,672	− 0·6	${}^4D^0_{\frac{1}{2}}$	50,654	0
${}^4D_{1\frac{1}{2}}$	75,035	0	${}^2D^0_{2\frac{1}{2}}$	49,012	0
${}^4D_{\frac{1}{2}}$	75,416	0	${}^2D^0_{1\frac{1}{2}}$	49,440	0
$(s^2p^4.6s)\ {}^2P_{1\frac{1}{2}}$	68,270	0	${}^2P^0_{1\frac{1}{2}}$	46,784	0
${}^2P_{\frac{1}{2}}$	66,838	− 1·2	${}^2P^0_{\frac{1}{2}}$	48,481	0
$(s^2p^4.5d)\ X_{1\frac{1}{2}}$	67,105	0	${}^2S^0_{\frac{1}{2}}$	47,847	0
$X_{\frac{1}{2}}$	65,788	0	$(s^2p^4.7s)\ {}^4P_{2\frac{1}{2}}$	38,550	+ 5·7
$(s^2p^4.6s)\ {}^2D_{2\frac{1}{2}}$	64,166	− 0·6	${}^4P_{1\frac{1}{2}}$	37,879	+ 5·4
${}^2D_{1\frac{1}{2}}$	64,163	− 0·6	${}^4P_{\frac{1}{2}}$	35,905	+ 0·3
$(s^2p^4.6p)\ {}^4S^0_{1\frac{1}{2}}$	59,277	0			

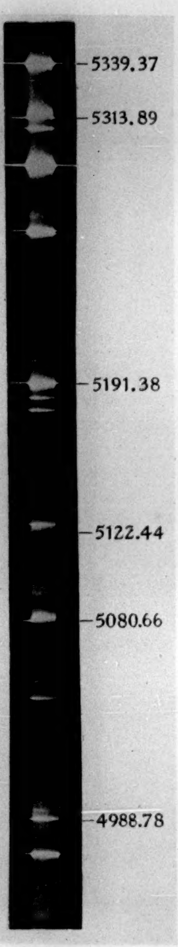
Table 3. Pressure displacements of the unclassified lines of the Xe II spectrum

Wave-length	Displacement (cm.⁻¹)	Wave-length	Displacement (cm.⁻¹)	Wave-length	Displacement (cm.⁻¹)
6994	− 0·8	4545·34	− 5·9	4238·37	− 8·2
6808	− 0·6	4541·03	− 4·5	4223·14	− 10
6705	− 1·0	4537·51	− 1·6	4209·75	− 6·0
6621	− 0·4	4537·02		4209·53	
6513	− 0·5	4486·12	− 0·5	4208·61	
6270	+ 0·6	4481·07	− 6·0	4193·25	− 7·0
6009	− 1·1	4462·38	− 7·7	4180·20	− 7·6
5616·99	− 0·3	4448·28	− 6·5	4158·14	− 5·1
5531·33	− 0·5	4395·91	− 6·0	4112·25	− 6·0
5188·28	large (−)	4393·34	− 5·4	4109·20	+ 0·6
5092·22	− 4·4	4369·34	− 5·4	4157·55	− 9·6
4853·90	+ 0·7	4337·14	− 0·9	3908·00	− 10
4773·34	− 0·7	4335·95	− 1·2	3849·97	− 8·2
4715·31	− 2·5	4330·63	− 7·6	3762·43	− 1·2
4698·20	− 3·0	4321·95	− 0·9	3720·93	+ 0·8
4668·72	− 1·2	4310·69	− 5·3	3717	− 1·5
4592·22	− 7·0	4296·52	− 2·9	3672·68	− 1·2
4585·65	− 6·2	4251·68	− 6·1	3612·52	− 0·8
4577·36	− 6·2	4245·54	− 7·3	3565·35	+ 0·8


a

b


c


d
5339.37
5313.89
5191.38
5122.44
5080.66
4988.78

The majority of the Xe II lines observed in the present investigation are not included in the classification by Humphreys, de Bruin and Meggers. But all these lines are included in a list of Xe II wave-lengths published by Bloch, Bloch and Déjardin*. Table 3 lists the lines which have measurable pressure displacements. The wave-lengths are those given by Bloch, Bloch and Déjardin and are the wave-lengths in air.

Table 3 shows that, in a general way, the displacements increase as we pass toward the shorter wave-lengths. This is an indication that the displacements are greater for levels with outer electron orbits.

§ 5. DISCUSSION OF RESULTS IN THE Xe II SPECTRUM

It has been generally supposed that the pressure displacements observed in ionized-gas spectra arise from internal electric fields. The present results for the Xe II spectrum support this view, inasmuch as the term displacements are found to be larger for terms of higher principal quantum numbers, a rule which in general holds for Stark displacements. From the present results, moreover, it is possible to say that, if the displacements arise from electric fields, these fields must be very large. For, certain of the Xe II lines have been observed† in electric fields as large as 100,000 V./cm. and they exhibit no measurable Stark displacements. Among these, for example, was the line λ 6093·53 which exhibits, in the present investigation, a large displacement (5 or 6 cm.$^{-1}$) toward the red.

The discrepant displacements occurring among members of certain multiplets of Xe II form an exception to the rule found by Pretty to hold in the A II and Ne II spectra: but they do not disfavour the hypothesis that the displacements are essentially a Stark effect, for Stark displacements are known to be governed by the arrangement of the terms in the energy diagram.

§ 6. DESCRIPTION OF THE PLATE

(*a*) Shows the Xe I line, λ 6318·08 ($2p_8$–$6d'_4$), broadened in the high-pressure source in comparison with the unbroadened line in the low-pressure source; (*b*) is a microphotometer record of the broadened line showing the asymmetry of the broadening; while (*c*) shows the Stark effect for the same line in fields attaining a maximum of 60,000 V./cm. (*d*) Shows some typical displacements in the Xe II spectrum, the central strip representing the high-pressure source.

§ 7. ACKNOWLEDGMENT

The writer has great pleasure in acknowledging the kindly interest which Prof. A. Fowler has taken in this work.

---

* *Ann. d. Phys.* (10), 2, 461 (1924).

† H. W. Harkness and J. F. Heard, *loc. cit.*

DISCUSSION

Prof. A. O. Rankine. I should like to raise the question of the use of the term "displacement" for the quantities recorded in the last columns of the tables, though I know that the author is not responsible for the choice of this nomenclature. The quantity has the dimensions of the reciprocal of a length, and the units are cm^{-1}. Scarcely anything could be more misleading than to call this a displacement when the same name in dynamics denotes a length, frequently measured in cm. The uninitiated would naturally take a pressure displacement to mean the shift of the spectral line on the spectrogram due to the application of pressure.

Author's reply. If the term "displacement" must always refer to a length then there is no escaping the contradiction here which Prof. Rankine points out between the name and the unit. However, I cannot agree that the use of this nomenclature must be confusing to anyone with a knowledge of spectra. One usually thinks of a spectral line on an energy level as a particular position in a continuum whose unit is the wave-number or cm^{-1}, and quite naturally, I believe, one thinks of a change of position as a "displacement."

DEMONSTRATION

677.31

"Infra-red photography of black or pigmented animal fibres." *Demonstration given on June* 16, 1933, *by* P. W. CUNLIFFE, Ph.D., F.R.P.S., Wool Industries Research Association.

The microscopic investigation of black wool and other pigmented fibres presents considerable difficulty, and any method which assists in rendering the fibre detail more obvious is therefore welcome. An advance in this direction has been made possible, by the use of infra-red photography, in the laboratories of the Wool Industries Research Association.

The presence of black hairs in the fleece, the remnant of the old hairy outer coat of the primitive sheep, is a disadvantage in the manufacture of wool fabrics, and its hairy or kempy nature has hitherto been difficult to establish or examine.

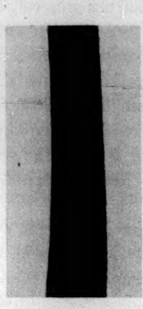


Figure 1. (× 165.)

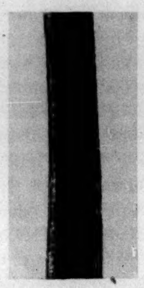


Figure 2. (× 165.)

The two photomicrographs reproduced herewith are of a black lamb fibre. Figure 1 is the rendering given by a panchromatic plate (Ilford S.G.) with a deep red filter (Wratten F.) and shows very little detail, giving an impression of an almost solid black filament, whilst figure 2 is from an infra-red photograph (Ilford plate and filter) and shows considerable detail. The fibre is medullated, and this indicates a kempy or hairy nature rather than a desirable wool characteristic. The photograph necessarily shows a black centre whatever the quality of the transmitted light.

Similar results have been obtained on other heavily pigmented fibres and hairs, such as kangaroo and negro hair.

PRESENTATION OF THE DUDDELL MEDAL, 1933

To Prof. WOLFGANG GAEDE

June 16, 1933

Prof. A. O. Rankine, President, in making the presentation said:

The Duddell Medal is awarded annually by the Council of the Physical Society to an inventor of physical instruments of outstanding importance and utility, or to a discoverer of new materials essential in their construction. There are no restrictions of nationality, and it is the duty of the Council each year to search the world to find the most worthy recipient.

The institution of the medal is comparatively recent, but I think it will be agreed that the short list of awards during the last decade has set a very high standard and that the illustrious names which it contains have been chosen well. To this list the Council with complete unanimity last December added another name, that of Dr Gaede whom we now welcome very warmly to receive the medal.

I am sure that it is unnecessary for me to explain the reasons for the choice which the Council has made. Gaede and vacuum are almost synonymous terms, and all physicists are well aware of his outstanding contributions to the art of vacuum-making and of how his wonderful pumps have facilitated physical investigations in innumerable directions.

In conclusion I must permit myself to remark that it has been a surprise and pleasure to discover that Dr Gaede is as young as he is. The name of his pumps has been so often on our tongues that most of us had perhaps begun carelessly to think of him as belonging to a previous generation. Now that we meet him in the flesh we rejoice to find ourselves mistaken, and we congratulate him on his comparative youth. We are sure that in the many years that lie before him his unsurpassed skill and ingenuity will continue to be at the service of physical science. With him in the forefront progress is certain to be made.

Professor Gaede, in the name of the Physical Society I ask you to accept this, the Duddell medal of 1933. It is a token of the esteem in which we hold you and your work. We desire to honour you as highly as we can, but we realize that in accepting our award you will be conferring on our Society a still greater honour.

Prof. Gaede, in accepting the medal, said:

It is hard for me to express in English how much touched and pleased I am to be in your midst and to be able to thank you in person for the great honour you have accorded me. This feeling is all the greater as in your award I see a practical sign of the international union of scientific work and of our co-operation. Therefore I express my heartiest thanks.

621.527.8

NOTE ON GAEDE PUMPS

In 1905 Gaede demonstrated at the scientific congress at Meran his newly produced air-pump, which in the main consisted of a porcelain drum divided into cells and rotating in an iron casing half filled with mercury. The advantages of this "rotary mercury pump" were simplicity of form, security, high vacuum and tenfold pumping speed. It therefore gained widespread popularity in laboratories and in electric-lamp factories.

Then Gaede applied himself to constructing various rotary oil air-pumps which first were to serve as fore pumps for the mercury pumps, and then were used as independent pumps. The principle of all these pumps had been brought into use by Otto von Guericke. A chamber alternately increases and decreases in volume. When increasing it draws air from the receiver which is to be evacuated, and when decreasing it compresses the enclosed air and puffs it out into the atmosphere or into the fore vacuum. Till then all pumps for laboratories and engine works, except jet pumps, were based on this principle; it was Gaede who in the years 1910–1915 worked out two new principles for the construction of air-pumps: the friction principle used in the molecular pump and the diffusion principle.

On the friction principle the pumping effect arises by air friction on the smooth surface of a spindle rapidly rotating in the middle of a cylindrical casing. The circular space between the cylindrical spindle and the cylindrical casing is interrupted by a projection fixed on the inner wall of the casing, so that the spindle may rotate freely at a distance of about 0·1 mm. from the projection. The rotating spindle produces by gas friction an effect of pressure in the surrounding gas so that between the sides of the projection a difference in pressure of a few millimetres arises. The essential point is that this difference is independent of the pressure itself, according to the kinetic theory of gases. If we lower the pressure itself beneath the value of the difference, we gain a high vacuum and a great pumping speed of more than one litre a second. A special advantage of this molecular pump is that it produces a vacuum free from any vapour. Although it constituted a great scientific and technical advance it was prevented from playing its part in full by the inventor himself, who superseded it by a new construction based on the diffusion principle.

On the diffusion principle air-free mercury vapour, produced in a small vessel with a reflux condenser, streams rapidly through a pipe. Into this vapour-pipe leads a suction pipe which is connected with the vessel to be evacuated. Mercury vapour enters the mouth of the suction pipe where it must at once be condensed in order to keep the vessel which is to be evacuated free from vapour. At the same time air leaves the mouth of the suction pipe and enters the vapour pipe where it is seized by the streaming mercury vapour and carried to the fore vacuum. In the mouth of the suction pipe, as we see, air and vapour move in opposite directions. The essential point of the diffusion principle is that the air shall diffuse through the countermoving vapour and not be pushed back by the vapour and thus prevented from entering the vapour pipe, as atmospheric air is pushed back by steam issuing from a boiler and is prevented from entering it. The difficult problem therefore was to bring about the diffusion of the air into the vapour and to avoid the prevention of its exit from the suction pipe. It was Gaede who solved this problem by rightly dimensioning the width of the mouth of the suction pipe. His experiments and calculations proved that the width of this mouth or slit must not exceed the free mean path of the gas molecules in the vapour at this point. This fundamental condition is fulfilled in all the high-vacuum vapour pumps which have subsequently been produced by different inventors and under different names. Not only the vacuum but also the pumping speed of these pumps is excellent. The reason lies in the correspondence between decrease of pressure and increase of the velocity with which the air diffuses through the vapour. In all these pumps, independently of their pumping speed, the velocity of the diffusing air is about 10 metres per second. The pumping speed is the product of this velocity and the area of the opening mentioned above. Gaede attained in his first pump a speed of about 0·1 litre per second and finished with about 400 litres per second. In his latest constructions he has used an improvement due to Langmuir, who unified Gaede's diffusion principle with the principle of the steam jet pump well known for its great speed. This improvement has been very generally introduced. Burch showed that the pumps might be worked advantageously with oil vapour of low pressure instead of mercury vapour.

REVIEWS OF BOOKS

Great Men of Science, by PHILIPP LENARD. Pp. xix + 389. (London: G. Bell and Sons, Ltd.) 12*s.* 6*d.* net. *Makers of Astronomy*, by HECTOR MACPHERSON. Pp. 244. (London: Humphrey Milford, Oxford University Press.) 7*s.* 6*d.* net.

Thumbnail biography is perhaps the most difficult of all the arts of the biographer, only to be approached at the other end of the scale by the intricacies of the task of transferring to a full-size canvas such an immense mass of heterogeneous material as confronted, say, Boswell or Lockhart. In each instance the individual traits, all the more interesting if they happen to be eccentricities, which elucidate character are to be sketched; in each instance the figure sketched must be placed against the background of his times, and his contribution to the advancement of the knowledge of his age duly explained and assessed. No easy matter, this, to achieve within the compass of a thousand pages—an almost impossible business to compress it within the limits of a thousand words. Nevertheless, many writers have attacked and accomplished such a task. What success has attended the effort of Prof. Lenard? He has, indeed, covered a most remarkable range—his roll of names opens with Pythagoras of Samos, closes with Friedrich Hasenöhrl and includes studies of sixty-five scientific worthies. Representatives of physical science naturally predominate, but he has not been unmindful of the claims of other branches of knowledge, and has provided us with sympathetic pictures of Darwin, Linnaeus, Dalton and Davy.

Perhaps the outstanding feature of his sketches is his quiet insistence on the difficulties which face the discoverer of a new concept—a matter all the more troublesome to make clear to the student of to-day to whom a concept novel and complex in 1831 is the merest commonplace a century later. Another valuable feature is provided in the intimate and informing sketches of such workers as Ohm, Oersted, Weber, Klaproth, Gauss and Carnot who, as far as their personalities are concerned, are names and nothing more to many English workers.

In brief notices, where every word must be weighed, an almost meticulous accuracy is demanded of the writer. It is unnecessary to stress the great care with which Prof. Lenard has weighed his words and the high standard of accuracy which he has set for succeeding writers. Nevertheless, the good Homer nods, on occasion, and Prof. Lenard leaves us with the impression that Copernicus swept away the whole complicated system of cycles and epicycles necessary to make a geocentric theory fit the facts of observation. Which he didn't; Copernicus was a thoroughly orthodox epicyclist, and the distinction of getting rid of that complicated theory is Kepler's. Nor was the charge of heterodox astronomical beliefs more than one charge among many that sent Bruno to the stake. The matter is not easy to elucidate, but Gaspar Schopp was present at the trial and his famous letter to Conrad Rittershausen gives as the damnatory clauses of the sentence Bruno's denial of transubstantiation and of the virgin conception, his publication of the *Bestia Trionfanti*, and lastly, his teachings concerning the lawfulness of magic, that Christ was not God, that the number of worlds was infinite and so forth. Bruno's astronomical teachings were among the least of the charges preferred against him. And did Joule die at Salford? But we must not seem ungrateful. Prof. Lenard has produced a series of charming and scholarly sketches which all may read with pleasure and with profit.

Dr Macpherson's task is easier; he has restricted himself to one field, that of astronomy, and he is consequently able to place his biographical studies in a more intimate relation to the majestic sweep of the development of his chosen science. He divides his studies into a series of well-marked sections—the pathfinders, Newton and after Newton, Herschel and his successors, pioneers of astrophysics, watchers of the skies, and explorers of the universe. His studies of the makers of astronomy open with the names of Copernicus and Tycho, close with those of Eddington, Shapley, van Rhijn and de Sitter. We may not accept his opening statement that "the first of the long list of great men who are entitled to the designation of makers of astronomy was born at Thorn on the Vistula on 19 February 1473," but our thanks are due to him for a learned and well-balanced sketch of the development of modern astronomy.

Both books are admirably produced and illustrated.

A. F.

Opticks, or a treatise of the Reflections, Refractions, Inflections and Colours of Light, by SIR ISAAC NEWTON. Pp. xxviii + 414. (London: G. Bell and Sons, Ltd.) 6*s.*

"Yes, my boy, the 1704 edition, not the suspicion of a crack in the joints, label intact, not a stain or a tear anywhere, in mint condition. And I picked it up for thirty shillings at Nith's." So might your dearest friend extol the beauties of his copy of the *Opticks* what time you remark, even as Johnson when peering at the beauties of Bennet Langton's grounds, "Non equidem invideo; miror magis."

The enterprise of the publishers has placed within the reach of those of us who have not been lucky enough to pick up a copy of the *Opticks* for thirty shillings, a means of making a first-hand acquaintance with the text of a very remarkable book. Nay, even the fortunate possessor of the 1704 edition may do well to purchase this handy volume. It will save him from committing the sacrilege of reading the original text.

The present edition is a reprint of the fourth edition (1730) "corrected by the author's own hand, and left before his death with his bookseller." The type is clear and pleasant to read, the illustrations well reproduced, the format a small octavo; and we have a foreword by Einstein and an introduction by Whittaker. Need one say more?

A. F.

The Anatomy of Modern Science, by BERNHARD BAVINK. Translated from German by H. STAFFORD HATFIELD. Pp. xiii + 683. (London: G. Bell and Sons, Ltd.) 21*s.*

More than a generation ago there issued from the press a work of great insight and magistral scholarship, *A History of European Thought in the Nineteenth Century*. That book influenced many workers powerfully, not so much by any profundity of original contribution as by the clarification of ideas resulting from the study of a masterly survey of all branches of thought. The mantle of John Theodore Merz has fallen upon Dr Bavink, who has produced a volume destined, we trust, to aid many who regard with growing bewilderment the ever-accelerating rate of advance of the sciences, physical and biological.

Dr Bavink's volume is divided into four sections. The first part deals in considerable detail with the facts and philosophy of modern physical science, the second part with "cosmos and earth." In the third part the facts and problems of biological science are handled and, just as part 2 places the notions of modern physical science in their relation to the cosmos, so part 4, on "nature and man," considers the cosmical implications of the facts of biology.

The book is not one to be read uncritically. We cannot, for example, subscribe to Dr Bavink's criticism of the conceptualist position as expressed in his italicized statement that "*Atoms are just as real things as cannon balls or grains of sand, as waves on water or mountains*." They remain what they always have been, integral parts of a conceptual world framed to represent the facts of sense-presentation. And if this concept is valid as an explanation of the pressure read on a Schräder gauge, it remains valid as an interpretation of that mark on a photographic plate known as an α-ray track. Multiply such phenomena by the million, and the atom remains just as much or as little "real" as it was in the days of Mach.

As we have remarked, the book must be studied with one's critical judgment ever alert. So read, it is a most stimulating and valuable contribution to modern thought.

The book is excellently produced, and its seven hundred pages do not lie over heavily in the hand.

A. F.

Matière et Energie, by V. Henri. Pp. 436. (Hermann, Paris, 1933.) 110 fr.

Prof. Victor Henri has given here a good and not difficult account of the present state of atomic physics, bringing the information up to the most recent discoveries about the nucleus. The book will be found specially convenient for the experimental physicist, who does not so much want detailed information about the abstruse mathematics of the new mechanics as a general review of the present state of knowledge. There are a great many useful tables of atomic constants of all kinds and there is a good deal of mathematics, but mostly of a simple type. The work is treated in a historical manner. The first chapter describes the evidence for the existence of atoms—Brownian movement and so on—and describes the various ways in which they can be counted. The next three chapters deal with the chemical elements, their X-ray spectra, the periodic system, atomic numbers, etc., and the next three with radioactivity, isotopes, nuclear disintegration and neutrons. There is then an account of the special properties of atoms, as revealed by X-ray crystal analysis and by gaseous viscosity. In the last chapter the structure of atoms is dealt with, mostly by the use of the old mechanics, though the new is sufficiently developed to explain the changes. Altogether the book should prove most useful for any one who wants to learn the main points of interest in modern physics, and the large number of tables given will also make it useful as a work of reference.

The Classical Theory of Electricity and Magnetism, by Max Abraham. Revised by Prof. Richard Becker. Translated by John Dougall, M.A., D.Sc., F.R.S.E. Pp. xiv + 285. (London: Blackie and Son, Ltd.) 15*s*.

"Abraham-Föppl" needs no introduction to European physicists—its merits have been known since 1894 to all interested in the development of Maxwell's theory. In the eighth German edition, of which the present volume is a translation, a number of alterations and additions have been made which, however, have left essentially unchanged the main features of a work which has become a classic. At the present juncture it is interesting to note that Prof. Becker remarks "In the choice of units...the system used throughout is the Gaussian system in which the energy density in a vacuum is equal to

$$\frac{1}{8\pi}(E^2 + H^2)\,\text{ergs/cm}^3$$

And the dielectric constant and permeability of a vacuum are each taken as unity. It does not seem possible at present to set up a system of units which will satisfy the electrical engineer and the physicist alike." The volume is divided into four parts. Part 1 is an admirable treatment of vectors and vector fields, part 2 deals with the electric field, part 3 with the electromagnetic field and part 4 with energy and forces in Maxwell's theory.

The translation flows easily, and it goes without saying that the book is admirably produced.

A. F.

***Relativité Générale; Gravitation et Électricité; Cosmologie*, by A. Einstein. Pp. 109. (Hermann, Paris, 1933.) 35 fr.**

This is a French translation from the German of three essays by Einstein. The first, which fills nearly two-thirds of the book, is devoted to the relativistic theory of gravitation. It follows the ordinary routine for the subject, developing the mathematical theory of tensors; it makes specially clear the distinction between the parts of the theory concerned with free space and the interior of matter. The second essay develops Einstein's new unitary theory, depending on the idea of "parallel displacement," and succeeds in doing it in only 26 pages. The whole theory is there, and the account would be useful to any one already fairly familiar with the ideas of advanced geometry, but it is to be doubted whether the beginner would make much of such a condensed account of a very abstract theory. The last essay is much more physical in its thought, and devotes 10 pages to a very good account of the theory of the expanding universe. The mathematical formulae contain rather too many misprints.

Théorèmes de Conservation dans la Théorie des Chocs Électroniques (Exposés de Physique Théorique IX), by A. Goldstein. Pp. 26. (Hermann, Paris, 1933.) 7 fr.

In the developments of wave mechanics there have been a good many of the simpler points which have been incompletely expounded, though it was always evident that they were completely in order. To any one familiar with the new mechanics the present work will hardly be necessary, but for a beginner it may be a convenience to see how the conservation theorems for collisions formally emerge from the theory.

Actualités Scientifiques et Industrielles. (1) No. 56, *Sur la Théorie du Rayonnement, d'après M. C. G. Darwin*, by E. Néculcéa; pp. 24; 7 fr. (2) No. 57, *Sur l'Absorption Exponentielle des Rayons β du Radium E*, by G. Fournier and M. Guillot; pp. 38; 10 fr. (3) No. 59, *La Diffraction de la Lumière par des Ultra-Sons*, by L. Brillouin; pp. 32; 10 fr. (Paris: Hermann et C^{ie}, 1933.)

(1) The first of these three numbers of the well-known French series of short monographs is a translation, rather than what we understand by an "analyse détaillée," of a recent paper by C. G. Darwin*. It will doubtless be of service to French readers, but most English readers will not unnaturally turn to the English original.

(2) In the second, MM. Fournier and Guillot present a critical discussion of earlier work on the absorption of β-rays by matter, together with an account of their own more recent work carried out at the Laboratoire Curie in Paris.

(3) In this paper M. Brillouin discusses in some detail the theory of the very interesting diffraction phenomena which are observable when light traverses a medium in which high-frequency elastic waves (supersonic waves) are maintained.

H. R. R.

Optik: Ein Lehrbuch der elektromagnetischen Lichttheorie, by Prof. Max Born. Pp. vii + 591; 252 figures. (Berlin: Julius Springer, 1933.) RM. 36; gebunden RM. 38.

In his presidential address to the Optical Society three years ago Mr Twyman pointed out that optics should no longer be defined as "a science which treats of light and the phenomena of vision," but rather as the science which deals with radiation, and he proceeded to show how some of the more recent developments of physics, such as wireless, X-rays, positive rays, etc. could with justice be included in the "optical empire." Although we have not reached the stage when a book is entitled, say, "Optics: Wireless Valve Transmitters," it is desirable that authors of books on optics should specify the branches with which they are dealing. Prof. Born has done this in the book under review, and in his preface he is careful to state quite specifically the limits within which he has confined the treatment of his subject and his reasons for choosing these limits; the choice appears to be a wise one. After a brief historical survey occupying eight pages, he divides the subject into eight sections: the electromagnetic theory of light for transparent isotropic substances without dispersion; geometrical optics; interference; diffraction; crystal optics; metal optics; molecular optics; emission, absorption and dispersion. The method of treatment is almost entirely mathematical, but can be followed by any one possessing a good knowledge of the theoretical aspects of optics. In his preface Prof. Born remarks that Drude's well-known book is one of the few scientific books which will always remain a classic. If this is true, the present book is also certain to rank as a classic. The author is to be congratulated on the clarity of his style and the publishers on the excellent manner in which they have produced the book.

---

* *Proc. R. S.* A, **136**, 36 (1932).

Actualités Scientifiques et Industrielles, No. 54. *Spectres d'Absorption Visibles et Ultra-violets des Solutions: Technique de leur emploi au laboratoire de Chimie*, par M. CHATELET. Pp. 24. (Paris: Hermann et C^{ie}, 1933.) 7 fr.

This monograph, the latest in a noteworthy series, presents very clearly and concisely the essential points in the photometry of absorption spectra, with particular reference to the methods adopted by the author himself. In addition to brief descriptions of certain apparatus, e.g. a water-cooled hydrogen tube as a source of ultra-violet continuum, several devices for diminishing spectrographic intensities in known ratios, and a microphotometer, the text includes a few useful notes on other practical matters, such as cements for absorption cells, choice and development of photographic plates, adjustment of apparatus, and the like. There is little or nothing to criticize, but it may be pointed out that twice on p. 3 the word "term" (*terme*) is wrongly used for "line" (*raie*). W. J.

The Practice of Spectrum Analysis with Hilger Instruments, sixth edition, compiled by F. TWYMAN, F.R.S. Pp. 58. (London: Adam Hilger, Ltd., 1933.) 3*s*. 6*d*. net.

The fifth edition of this useful and attractive booklet* is followed by a sixth after an interval of only twenty-one months. The size of the manual and the titles of the chapters are little changed, but the text has been very thoroughly revised by Dr A. Harvey, whose name and Mr E. S. Dreblow's are now added to the list of names of contributors. Space has been found for much useful new matter by rearrangement and condensation of older material and the deletion of a few sections whose period of usefulness is now over. For example, the bibliography which formed the third and last appendix in the fifth edition is now omitted, and references formerly included in it and in the text are now given in footnotes. Much of the change occurs in the chapter on quantitative spectrum analysis, which now contains discussions of the application of logarithmic wedge sector, the ratio powder method, etc. In other chapters new matter occurs in the form of notes on preliminary treatment of specimens, the effects of polarity in arcs between poles of unlike composition, the characteristics of photographic plates, etc. W. J.

---

* Reviewed in *Proc. Phys. Soc.* **44**, 108 (1932).

Spectroscopy in Science and Industry, by S. JUDD LEWIS, D.Sc., F.I.C., Ph.C. Pp. viii + 94 and 10 plates. (London and Glasgow: Blackie and Son, Ltd., 1933.) 3*s*. 6*d*. net.

This is an "introductory manual" in Blackie's *Technique Series* describing the applications of spectrographic methods in industrial and other practical problems, especially the qualitative and quantitative spectrum analysis of substances. It is not concerned with the description and analysis of spectra, the subject for which Sir Arthur Schuster proposed the name "spectroscopy." The instruments described are all by Messrs Adam Hilger, Ltd. Some of these are shown in figures in the text and in plates; in the rest of the plates spectrograms taken with Hilger instruments are beautifully reproduced. In many respects the text is disappointing, although it has some interesting sections. If the length of this review permitted, it would be only too easy to cite many instances of unordered treatment, loose expression and actual mis-statement, which the elementary and empirical nature of the descriptions can hardly be said to excuse. Compared with such blemishes, the appearance of "ultimate rays" on pp. 29 and 35 as a rendering of "*raies ultimes*," and "Molesey" on p. 88 for "Moseley" are mere trifles.

W. J.

High-Frequency Measurements, by A. HUND. Pp. xi + 491, with 373 diagrams. (McGraw-Hill Book Co., London and New York, 1933.) 5 $.

The work is divided into eighteen chapters, of which the first three serve as a general introduction to the subject, giving summaries of fundamental relations, of the more important properties of high-frequency circuits, and of methods for the production, detection and measurement of rapidly alternating currents, with other information of a general nature. Of the remaining fifteen chapters, each one as a rule deals with the measurement of one particular quantity—voltage, frequency, capacitance and so forth—or of sets of closely associated circuit constants.

A good selection of methods is given, and a compilation of this kind, in a subject of which the literature is so widely scattered in scientific and technical journals, cannot fail to fulfil a very useful purpose. It should be valuable not only to all engaged regularly in high-frequency measurements, but also to the large general body of physicists with no more than an occasional interest in such work. Readers of the latter class in particular will find the subject-matter admirably arranged for easy reference.

The alphabetical index (27 pp.) is if anything too grimly comprehensive; thus, a brief section of a minor footnote (on p. 35) is indexed no fewer than six times, under "Bohr, energy levels," "Born energy levels," "Heisenberg, W., on spectroscopy," "matrix calculus," "Pauli, on spectroscopy" and "spectroscopy"—roughly one reference to each line of the text—but this is rather an extreme example. A few slips and misprints point to a rather hurried completion of the text—the references to one "K. Omnes," a worker on electrical conductivity of metals at low temperatures, provide one of the more striking examples of this.

In the second edition, which will doubtless be called for very soon, it would be a boon to readers of subnormal, and even of normal, eyesight if the otherwise excellent diagrams could be printed on a larger scale, even though this could not be done without an appreciable increase in the size and price of the volume.

H. R. R.

Gas Analysis by Measurement of Thermal Conductivity, by H. A. DAYNES, D.Sc. (Cambridge University Press.) 16*s*.

To certain present-day scientific workers the term "katharometer" bears something of the significance to the old lady of that blessed word Mesopotamia—high sounding and comfortable but deeply mystic in meaning. It conjures up to their imagination the key to the solution of the most difficult measurements.

A glance through the present volume certainly impresses one with the versatility of the "katharometer" as a tool in the hands of the physicist, chemist and biologist. We are told that by means of it the quantity of carbon dioxide given off in the respiration process of a fly can be measured, and that this amounts to about half a cubic centimetre in six hours. It is, however, in the industrial field of gas analysis that the "katharometer" has come into its own, and according to the author of this volume many thousands of these instruments are in use for the measurement of the composition of flue gases from power house boilers.

Yet the hot wire method is not without its drawbacks, and Dr Daynes has done a real service by writing this comprehensive treatise on the instrument. His material has largely been drawn from experience in applying this method of gas analysis to practical problems and the fact that the manufacturers of the instrument in this country have allowed him unrestricted use of information obtained in the course of development work reflects great credit on them for their public spirit.

In his historical introduction the author traces the early stages of the development. It appears that Leon Somzee originated the device of analysing a gas by determining its conductivity about 53 years ago, but it did not reach the stage of successful application for many years. Other names that stand out conspicuously for their contributions towards making the method a practical success are those of Koepsel and Shakespear.

A student contemplating using this method in an investigation will find the volume a mine of information, for it deals with all aspects of the subject, including accessory apparatus. A feature of interest in the book is the description given of efforts to circumvent the limitation imposed by the fact that gases do not differ very greatly in thermal conductivity except in the case of hydrogen and helium.

The printing of the book and the illustrations are admirable and reflect credit on author and publishers.

EZER GRIFFITHS

Collision Processes in Gases, by F. L. ARNOT. Pp. viii + 104. (London: Methuen and Co., 1933.) (Methuen's Monographs on Physical Subjects.) 3*s*.

The book deals mainly with work in which individual collision processes are more or less directly studied. Part 1 discusses collisions between electrons and atoms, part 2, in two short chapters, collisions between photons and atoms, and between normal, excited, and ionized atoms. This deliberate limitation of the thesis has made it possible to give, in one small volume, a connected account of a fairly wide range of the more important and more readily interpretable of collision phenomena.

Students reading for honours degrees in physics will find here concise accounts of such topics as critical potentials, probabilities of excitation and ionization by electrons, the Ramsauer effect, and the numerous applications of Klein and Rosseland's "collisions of the second kind"—all well adapted to serve as convenient introductions to more detailed study. As would be expected, Dr Arnot, within his obvious limitations of space, deals particularly fully with the recent beautiful work on the scattering of electron beams by gases at low pressures.

The book is to be recommended as a valuable and timely addition to this useful series of monographs.

H. R. R.

Experimental Atomic Physics, by G. P. HANWELL and J. J. LIVINGOOD. Pp. xiii + 472. (London: McGraw-Hill Publishing Co., Ltd.) 30*s*.

This work is a very important contribution to pedagogical literature. The authors have concentrated on the experimental side of their subject, and their book contains descriptions of an admirable collection of laboratory exercises in atomic physics which should prove of great value alike to teacher and to student.

The book is, however, much more than a laboratory manual. It is an introduction to the subject, presented from the experimental side and intended to be read by those who have already had a course of elementary training in the classical aspects of physics. Although "a working knowledge of the calculus and of differential equations is... presupposed" the mathematics employed in the book is quite elementary in character. The topics treated of are developed logically and carefully and are, in the order of presentation, radiation, the atomicity of matter and electricity, the wave aspect of matter, thermionic and photoelectric effects, spectra, X-rays and radioactivity.

The book may be recommended unreservedly.

An Elementary Introduction to Physics, by EDGAR BOOTH. Pp. xvi + 465. (Glebe, N.S.W.: Australasian Medical Publishing Co., Ltd. London: H. K. Lewis. 1932.)

The author in his introduction indicates a feeling that his book will be criticized as not being up to date. It is certainly in the older tradition, many of the methods and verbal illustrations being reminiscent of a former generation of text-books. The study of mensuration and attention to accuracy of measurement are emphasized; mass and weight are not confused in one hybrid formula; proofs tend to be algebraic rather than geometrical; magnetism and electricity are the last subjects treated and together occupy one-ninth only of the book; modern physics is dismissed, if not with a shrug, at least with an electron and a paragraph; the cartesian diver reascends; levers are in systems one, two and three; the Grove cell still has its place between Daniell and Bunsen. Both the strength and weakness of the older tradition are present, but the virtues predominate. The general impression is that of sound teaching, and any student who knows the book well is well prepared to enter upon a course of London Intermediate standard. Upon general and historical topics the text is readable and informative. In this country school teachers may not discover anything very new in the book; but as an auxiliary text-book for those university students—and they are many—who read for science or medicine without previous acquaintance with physics the book may very well be recommended.

J. P. A.

Examples in Physics, by W. G. DAVIES. Pp. 128. (London: Edward Arnold and Co.)

This little book marks, in one way, a further stage in the evolution of its species. With regard to subject divisions the old books were casual, while their descendants developed definite sections devoted to the main branches of physics. The book shows, in addition, clear and adequate subdivisions. As a result, provided unconventionality is not sought, an example of any desired type may be found very speedily in one of the 25 subsections on general physics, the 12 subsections on heat, or elsewhere. The 580 examples themselves, many of which come from examination papers (although the source of individual questions is not indicated) are well up to the standard of Higher Certificate and London Intermediate examinations. They do not consist solely of numerical examples. A noteworthy, and on the whole up to date, collection which may be recommended to teacher and student.

J. P. A.

(1) *Professional Papers of the Air Survey Committee*, No. 8. *A Simple Method of Surveying from Air Photographs*. By Lieut. J. S. A. SALT, R.E. Pp. 145; 46 figures, 5 plates and 4 sheets. 4*s*. net. (2) *Parallax Tables*. Supplement to the above. Pp. 82; 2 figures. 1*s*. 6*d*. net. (London: H.M. Stationery Office, 1933.)

(1) In a short preface Col. Macleod, the Chairman of the Air Survey Committee,

points out that the type of aerial survey to which the Committee has given most attention is that which aims at the production of "fully contoured maps of moderate though sufficient accuracy, based on a limited ground control and making use of comparatively simple instruments." The previous seven Professional Papers published by the Committee described from a somewhat theoretical viewpoint the technique developed: the present paper presents a more practical description. It is divided into thirteen chapters entitled "introduction," "characteristics of air photographs," "photography," "ground control," "stereoscopy," "effect of small tilts on vertical photographs," "minor control plotting," "compilation of blocks," "detail plotting," "contouring," "reproduction," "rapid map production" and "mosaics." There is also an index giving a summary of terms used in aerial survey, with references to the Professional Papers. The monograph is well written and is sure to prove of great value to those who are concerned with the practical aspects of aerial survey.

(2) The parallax tables have been compiled to simplify the computation of the relationship between parallax and heights when contours are being plotted with the aid of a simple stereoscope.

The Scientific Journal of the Royal College of Science, vol. III. Pp. 120. (London: Edward Allen and Co.) 7*s.* 6*d.*

With the appearance of this, its third annual volume, the *Scientific Journal of the Royal College of Science* may be regarded as well established. It gives varied and good fare to its readers, and we trust that it will attain the wide circulation which it merits.

The present volume, which is divided into three sections, offers to the chemists five papers dealing with surface reactions, chemical synthesis in plants, the treatment of mineral oils, the structure of dyestuffs and the contribution of the chemist to industry. The natural-history section has two papers, one dealing with hibernation and the other with the development and classification of vegetation. In the physical section are contributions concerned with loud-speaker diaphragms, the disintegration of atoms by fast protons, the uses of high speed cathode rays, and uniform columns in electric discharges. The names of the distinguished authors of many of the papers are sufficient guarantee of the critical and scholarly treatment of the various themes.

A. F

THE PROCEEDINGS OF
THE PHYSICAL SOCIETY

VOL. 45, PART 6 *November* 1, 1933 NO. 251

537·362 : 546.56–8

ELECTRO-ENDOSMOSIS AND ELECTROLYTIC WATER-TRANSPORT

PART 3. SOLUTIONS OF COPPER SALTS

BY H. C. HEPBURN, PH.D., Birkbeck College

Received June 26, 1933

ABSTRACT. This paper gives the results of measurements of the liquid-transport produced by passing an electric current through aqueous solutions of cupric chloride and of cupric nitrate, the solution in each case being symmetrically divided by means of a parchment-paper diaphragm perpendicular to the direction of the flow of electricity. The results are considered in relation to data obtained previously by the author in the case of solutions of copper sulphate; and the electro-endosmotic effect of the parchment-paper diaphragm is discussed in terms of the influence of the electrical charge of the diaphragm and of the thickness of the electrical double layer formed at the interface diaphragm-aqueous solution.

The results obtained with the solutions of cupric chloride show that the direction of liquid transport is reversed in the case of the more concentrated solutions, and evidence is adduced suggesting that this reversal is attributable to the effect of the electrolytic water-transport.

§ 1. INTRODUCTION

THE author has previously* investigated the electrolytic water-transport in the case of copper-sulphate solutions by means of the parchment-paper diaphragm method. At the same time, the electro-endosmotic effect of the parchment-paper diaphragm and its dependence on the electrolyte concentration were examined. In the present work the investigation has been extended to solutions of cupric chloride and of cupric nitrate, so that the work embraces solutions of the cupric salts of the three common mineral acids. In the case of cupric nitrate, however, it was not found practicable to obtain satisfactory results with solutions of concentrations exceeding 0·0464-normal owing to disturbances introduced by a chemical action which accompanied the electrolysis.

---

* *Proc. Phys. Soc.* **43**, 524 (1931); *ibid.* **44**, 267 (1932).

The electro-endosmotic effect of the parchment-paper diaphragm, which becomes prominent in the case of the dilute solutions, is discussed in the light of experimental data obtained previously by the author and by other workers. The influence of (*a*) the electrical charge of the diaphragm, and of (*b*) the thickness of the electrical double layer (formed at the interface diaphragm-aqueous solution) is considered by means of a method proposed by the author in former papers*.

The results obtained with the solutions of cupric chloride show that the direction of liquid transport is reversed in the case of the more concentrated solutions; and evidence is adduced suggesting that this reversal is attributable to the effect of the electrolytic water-transport.

§ 2. EXPERIMENTAL

The apparatus employed, which was similar to that described by the author in a former paper†, consisted of two electrode chambers (one open to the air and the other closed) separated by a diaphragm of parchment paper. The liquid-transport across the diaphragm, when an electric field was applied at the electrodes, was determined, as in the previous work, by observing the movement of the liquid thread in a capillary tube attached to the closed electrode chamber.

The apparatus was immersed in an electrically heated water bath with a thermostatic device arranged to provide a temperature-control within the limits 18 ± 0·1° C.; and to avoid thermometric effects no heat was supplied to the tank immediately before or during the course of the flow-measurements. A higher working temperature (22·0° C.) was necessitated in the case of 0·0464-normal cupric-nitrate solution, as the room temperature during the measurement with this solution exceeded 18° C. Control experiments have indicated, however, that the variation in the liquid-transport per faraday over the temperature range 18·0° C. to 22·0° C. is less than the limit of experimental error (between 1 and 2 per cent).

As in the previous work, reversible copper electrodes were employed. A potential-difference of 20 V. was applied at the electrodes in the case of solutions of concentrations 0·1-normal and less, but at higher concentrations it was found desirable to adopt a lower voltage (6 V.) in order to minimize the possibility of disturbances arising from electrode reactions.

Determinations of liquid-transport were carried out with the solutions in order of increasing concentration. At the completion of the series of measurements with the cupric-chloride solutions the parchment-paper diaphragm was changed, and a further series of measurements made with the cupric-nitrate solutions. The employment of an entirely fresh diaphragm for each series of measurements obviates the difficulty, as the author‡ has pointed out, of removing by a washing process the last traces of adsorbed electrolyte from the diaphragm.

The experimental method adopted to measure the rate of liquid-transport differed slightly from that previously followed by the author. The meniscus, after traversing approximately 1 cm. of the capillary tube, was timed over a further 1 cm. of the tube (the time for the half cm. being taken also for purposes of checking), the potential-difference at the electrodes being applied in a given direction. The direction of the applied potential-difference was reversed when the meniscus had traversed a further 1 cm. of the tube, the meniscus, moving in the reverse direction, being again timed over the selected 1 cm. length.

---

* *Proc. Phys. Soc.* **38**, 363 (1926); *ibid.* **39**, 99 (1927).

† *Ibid.* **43**, 525 (1931).

‡ *J. Chem. Soc.* 3163 (1927).

If the initial movement is towards the end of the capillary remote from the apparatus, v_f, the liquid-transport per faraday, is given by the following expression:

v_f

$$v_f = [(1/T_1 - 1/T_s)(1/I_1)(0{\cdot}00973)(96{,}540)] - [C] \qquad \ldots\ldots(1),$$

where T_1 (sec.) is the observed time of liquid-transport per cm., T_s (sec.) the time of gravitational movement per cm. outward, I_1 (A.) the mean current through the diaphragm, 0·00973 the volume of the capillary in cm.^{3} per cm. and C the correction for the heating effect of the current* expressed in cm.^{3} per faraday. The corresponding expression for the liquid-transport on reversal is as follows:

T_1, T_s
I_1
C

$$v_f = [(1/T_2 + 1/T_s)(1/I_2)(0{\cdot}00973)(96{,}540)] + [C] \qquad \ldots\ldots(2),$$

where T_2, I_2 correspond with T_1, I_1.

T_2, I_2

Adding (1) and (2), we obtain the following expression for v_f:

$$v_f = \frac{K_1}{2}\left(\frac{1}{T_1 I_1} + \frac{1}{T_2 I_2}\right) + \frac{K_1}{2T_s}\left(\frac{1}{I_2} - \frac{1}{I_1}\right) \qquad \ldots\ldots(3),$$

K_1 being the product $0{\cdot}00973 \times 96{,}540$. The second term on the right-hand side of equation (3) may in general be neglected, the correction introduced in the present measurements being considerably less than 1 per cent except in the case of 0·5-normal (correction 11 per cent) and 1·0-normal (correction 8 per cent) cupric-chloride solutions where the values of I_1 and I_2 (see table 1) are somewhat divergent. Thus a precise measurement of the gravitational movement is in general unnecessary, and the correction for the heating effect of the current is eliminated†.

K_1

Control experiments showed that it was not essential in all cases to change the solution before making the reverse measurement of the liquid-transport, but this step was found desirable with the more concentrated solutions (e.g. those of 0·1-normal concentration and greater concentrations) in order to minimize the possibility of disturbances arising from reactions at the electrodes and from concentration-changes accompanying prolonged electrolysis.

Cupric-chloride solutions. Solutions of concentrations ranging from 0·0005-normal to 1-normal were employed, all of them being prepared by dilution from standard 2-normal solution. Analytical reagent cupric chloride was employed to prepare the standard solution, the concentration which was checked by the potassium-iodide, sodium-thiosulphate method of volumetric estimation. The sodium-thiosulphate solution employed in this estimation was standardized against a solution of analytical-reagent copper sulphate.

Preliminary observations showed a rapid diminution in the current, soon after completion of the circuit, in the case of solutions of 0·2-normal concentration and greater concentrations; a similar effect was obtained when the diaphragm was removed from the apparatus. The effect was accompanied by the deposition on the anode of an insoluble substance (probably an insoluble basic salt of copper formed by a secondary action at the electrode), the effective surface area of the electrode (and consequently the magnitude of the current also) diminishing progressively as deposition occurred. After the initial stage, however, the rate of current-diminution became less rapid; and sufficiently steady current-values were obtained, when a potential difference of 6 V. was applied at the electrodes, to enable measurements of liquid-transport to be made. No material variations in the current-values and in the rates of liquid-transport were observed in the case of solutions of concentrations 0·1-normal and less.

---

* See *Proc. Phys. Soc.* **43**, 529 (1931).

† The author previously employed equation (1) to determine v_f.

Cupric-nitrate solutions. A standard solution of approximately 1-normal concentration was made up, Kahlbaum's "purest" cupric nitrate being employed. The precise concentration of the standard solution was found by volumetric estimation to be 0·928-normal, and the solutions employed were prepared by dilution from this solution.

In the case of solutions of concentrations greater than 0·0464-normal, evolution of gases from the cathode was observed, the free nitric acid present (in consequence of hydrolysis of the solution) apparently reacting with the deposited copper and liberating nitrogen and certain oxides of nitrogen. The electrode reaction referred to appeared to introduce irregularities in the rate of liquid-transport, and no satisfactory results were obtained in the case of solutions of concentrations greater than 0·0464-normal; at the lower concentrations (0·000464-normal to 0·0464-normal), however, control measurements indicated practically uniform rates of liquid-transport.

§ 3. RESULTS AND CONCLUSIONS

The experimental results are given in tables 1 and 2.

The liquid-transport v_f in cm.^{3}/faraday is calculated by means of equation (3)*.
I_m I_m (column 9 of tables 1 and 2) is the mean of I_1 and I_2. The values given for the specific conductivity λ have been obtained by large-scale graphical interpolation from the data of A. Heydweiller† and of H. C. Jones‡.

v_f is shown in the tables as positive where the direction of liquid-transport is from anode to cathode.

The liquid-transport per faraday. The relation between the liquid-transport v_f per faraday and the electrolyte dilution is shown graphically in figure 1; the curve for solutions of copper sulphate has been added for purposes of comparison. In each case the values of v_f, over the dilution range 20 to 1000, lie satisfactorily on a smooth curve; and the value for dilution 2000 (or dilution 2155 in the case of the cupric-nitrate solutions) lies above the extension of the curve. The values of v_f

---

* See p. 757.

† Landolt-Börnstein, *Tabellen*, p. 1086 (1923).

‡ *Ibid.* p. 1092. Temperature coefficients have been computed by the author from the data of Heydweiller and Jones in order to obtain values of λ appropriate to a temperature of 18° C.

in the case of copper-sulphate solutions are higher than those relating to solutions of cupric chloride and of cupric nitrate. In the two latter cases the values lie fairly closely together, but certain differences are exhibited (see p. 763). No linear law, similar to that relating to the case of a powdered-glass diaphragm and copper-sulphate solutions of dilutions 10 to 200*, or to the case of a parchment-paper diaphragm and potassium-chloride solutions of dilutions 10 to 100†, is applicable to any of the present cases.

Table 1. Cupric-chloride solutions

Concentration (gm.-equiv./litre)	Current I_1 (A.)	Current I_2 (A.)	Time T_1 (sec.)	Time T_2 (sec.)	Liquid-transport v_f (cm.³/faraday)	Applied potential difference (V.)	Specific conductivity λ (reciprocal ohms)	$I_m/\lambda V$
0·0005	0·000832	0·000800	710·0	1130·7	1318	20·5	0·0000625	0·637
0·001	0·001503	0·001536	476·5	738·3	1069	20·5	0·0001134	0·653
0·002	0·002947	0·002965	327·6	512·5	796	20·5	0·0002162	0·667
0·005	0·00724	0·00721	262·5	366·4	425	20·4	0·000518	0·684
0·01	0·01396	0·01398	245·2	351·7	233	20·5	0·001007	0·677
0·02	0·02649	0·02659	254·4	456·2	108	20·4	0·001934	0·673
0·05	0·0621	0·0608	519·2	2250	18·0	20·3	0·004495	0·674
0·1	0·1175	0·1150	− 750	− 232·5	− 22·9	20·5	0·00833	0·681
0·2	0·0256	0·02635	27000	− 680·5	− 25·6	6·15	0·01544	0·273
0·5	0·0151	0·0092	3440	−1198	− 29·9	6·19	0·03355	0·058
1·0	0·0169	0·0107	2122	− 900	− 32·8	6·13	0·0569	0·039

Table 2. Cupric-nitrate solutions

Concentration (gm.-equiv./litre)	Current I_1 (A.)	Current I_2 (A.)	Time T_1 (sec.)	Time T_2 (sec.)	Liquid-transport v_f (cm.³/faraday)	Applied potential difference (V.)	Specific conductivity λ (reciprocal ohms)	$I_m/\lambda V$
0·000464	0·000665	0·000665	838·5	1308·8	1381	20·4	0·0000518	0·629
0·000928	0·001364	0·001393	607·0	696·0	1050	20·4	0·0001028	0·658
0·001856	0·002720	0·002767	406·7	456·8	795	20·4	0·0002027	0·663
0·00464	0·00669	0·00680	301·4	368·6	420	20·4	0·0004918	0·673
0·00928	0·01317	0·01341	248·6	316·9	254	20·4	0·000948	0·687
0·01856	0·02522	0·2548	216·6	306·6	146	20·3	0·001815	0·688
0·0464	0·0637	0·0621	272·4	1310·0	32·8	20·2	0·004422	0·704

The reversal of liquid-transport with cupric-chloride solutions and the apparent discontinuity in the curve between dilutions 10 and 20 (see figure 1 *A*) are discussed on pp. 763, 764.

The electro-endosmotic effect of the parchment-paper diaphragm. In order to examine the electro-endosmotic effect of the parchment-paper diaphragm in the light of the classical theory‡, it is necessary to obtain values for the electro-endos-

---

* H. C. Hepburn, *Proc. Phys. Soc.* **39**, 99 (1927).

† H. Remy, *Z. Electrochem.* **29**, 365 (1923).

‡ Helmholtz, *Wied. Ann.* **7**, 337 (1879). See also M. v. Smoluchowski's monograph on electro-endosmosis in Graetz's *Handbuch der Elektrizität und des Magnetismus*, Bd. **2** (2), p. 366 (1914).

v motic liquid-transport v produced by the application across the diaphragm of a constant potential difference. Subject to certain limitations discussed by the author in a former paper*, v is given by the following expression:

$$v = K_2 (v_f - H) \lambda \qquad \ldots\ldots(4),$$

v_f, H where v_f is the observed liquid-transport per faraday, H the electrolytic water-
λ, K_2 transport per faraday, λ the specific conductivity of the electrolyte solution, and K_2 a constant.

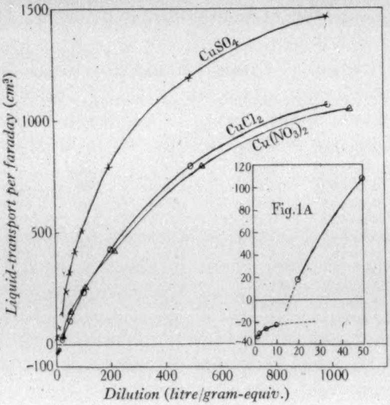


Figure 1. Liquid-transport per faraday. An enlargement of the lower part of the $CuCl_2$ curve appears in figure 1*A*.

I_m, V Equation (4) implies a proportionality between the specific conductivity λ and the mean current I_m flowing through the diaphragm when a given voltage V is applied at the electrodes. Values of $I_m/\lambda V$ are given in tables 1 and 2, column 9, and are seen to be practically constant over the concentration range 0·005-normal to 0·1-normal in the case of cupric-chloride solutions, and over the concentration range 0·00464-normal to 0·01856-normal in the case of cupric-nitrate solutions. The somewhat lower values of $I_m/\lambda V$ in the case of concentrations less than 0·005-normal (cupric chloride) or less than 0·00464-normal (cupric nitrate) suggest a diaphragm polarization effect†; the lower values in the case of 0·2-normal, 0·5-normal and 1·0-normal cupric-chloride solutions, however, appear to be due mainly to the effect referred to on pp. 757, 758 and not to diaphragm-polarization.

H appears to be negative in the case of cupric-chloride solutions (see p. 764), interpolation of the curve of figure 3, which shows the relation between H and concentration, giving values for H which range from − 18·7 cm³ in the case of 0·0005-normal solution to − 22·9 cm³ in the case of 0·1-normal solution. The values of H thus obtained have been employed to compute the expression $(v_f - H)\,\lambda$, which is plotted against concentration in figure 2. It may be pointed out, however, that if a constant value for H is assumed over the concentration range 0·0005-normal to 0·1-normal no material error is introduced. In the case of copper-sulphate solutions, the evidence adduced by the author* in a former paper suggests that H is here positive and approximately constant at concentrations not greater than 1-normal. The expression for v/K_2, equation (4), appropriate to this case, viz. $(v_f - 29{\cdot}3)\,\lambda$, is also plotted in figure 2 for purposes of comparison.

---

* *Proc. Phys. Soc.* **43**, 534 (1931).

† *Ibid.* **44**, 267 (1932).

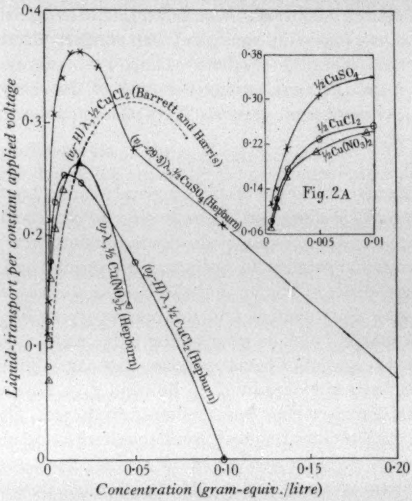


Figure 2. Liquid-transport per constant applied voltage across the diaphragm. Figure 2*A* shows the rising branches of the curves in greater detail.

Values of H are not available in the case of the cupric-nitrate solutions, the curve given in figure 2 for these solutions representing the expression $v_f\lambda$; i.e. no correction is applied for the electrolytic water-transport. If, however, a correction is applied of the same magnitude as that appropriate to the cupric-chloride solutions or to the copper-sulphate solutions, the order of the rising branches of the three curves remains unchanged up to concentration 0·005-normal.

The values of $(v_f - H)\,\lambda$ (or of $v_f\lambda$ in the case of the cupric-nitrate solutions) for concentrations 0·002-normal (or 0·001856-normal in the case of the cupric-nitrate solutions) and less lie in each case on the lower part of the rising branch of the curve, the possible disturbances produced by diaphragm polarization (see p. 760) apparently having little effect on the general form of the curves.

---

* *Proc. Phys. Soc.* **43**, 533 (1931).

Variations in the form of the (v, concentration) curve obtained with a given solution appear to arise when different specimens of parchment paper are employed as diaphragms, e.g. the curve obtained from the data of J. O. W. Barrett and A. B. Harris* for solutions of cupric chloride differs from that given by the author's results; see figure 2. These variations are probably attributable to differences in the electrolyte content, texture, etc., of the parchment paper employed; all the diaphragms employed in the present work were therefore cut from the same sample of parchment paper so as to ensure that the results obtained with different solutions should be strictly comparable.

The curves of figure 2 show that v, in each case, increases initially with increasing concentration, attains a maximum value, and then regularly decreases. In order to trace the factors which contribute to these maxima, it is convenient to examine the
e relation between v and the mean surface density e of the charge on the walls of the parchment-paper diaphragm channels. This relation, according to the classical theory, is as follows:

$$v = (K_3/\eta)\,\delta . e \qquad \ldots\ldots(5),$$

δ where δ is the effective thickness of the electrical double layer at the interface
K_3, η diaphragm-solution, K_3 is a constant, and η is the viscosity coefficient, which may be regarded as a constant in the case of the dilute solutions here considered.

It has not been found practicable, owing to experimental and other difficulties, to examine the dependence of δ and e on the electrolyte concentration in the case of the parchment-paper discs employed in the present work; but the author† has devised a method enabling such an examination to be made in the case of electro-endosmotic measurements with a powdered-glass diaphragm. This method, suitably modified, has since been employed by H. B. Bull and R. A. Gortner‡ in the case of streaming-potential determinations with a cellulose diaphragm. The author obtained maxima in the (v, concentration) curves§, similar to those found in the present work (figure 2), in the case of the electro-endosmotic flow of aqueous solutions of potassium chloride, hydrochloric acid and barium chloride through powdered glass. There were also maxima in the (δ, concentration) curves, but the diaphragm charge e increased with increasing concentration except in the case of solutions of potassium chloride, where a slight initial decrease followed by a regular increase appeared.
ζ The results of Bull and Gortner are expressed in terms of ζ, the interfacial potential-difference of the electrical double layer, which is usually taken as proportional to v in the case of dilute solutions. Bull and Gortner find maxima in the case of the (ζ, concentration) curves relating to aqueous solutions of potassium chloride, sodium chloride, potassium carbonate and potassium sulphate. The corresponding (δ, concentration) curves indicate that δ decreases continuously with increasing concentration, except in the case of solutions of sodium chloride and potassium

---

* *Z. Elektrochem.* **18**, 221 (1912).

† *Proc. Phys. Soc.* **38**, 363 (1926); *ibid.* **39**, 99 (1927).

‡ *J. Phys. Chem.* **35**, 309 (1931).

§ Values were plotted of ζ, the interfacial potential-difference of the electrical double layer, which was taken as proportional to v.

sulphate, where slight maxima appear. The maxima in the (ζ, concentration) curves were accompanied in all cases by regular increase in the diaphragm charge, this result corresponding with that obtained by the author with the powdered-glass diaphragms. Proceeding by analogy, it thus seems probable that the maxima in the (v, concentration) curves, obtained in the present work with the parchment-paper diaphragms, arise from the simultaneous effect of increasing diaphragm charge and decreasing thickness of the electrical double layer, modified to some extent by initial increase in the latter quantity. In this connexion, it may be observed that cellulose appears to bear a closer relation to parchment paper than does powdered glass, and in the cases recorded by Bull and Gortner for cellulose the modifying factor referred to is not of great effect.

The curves of figure 2, taking the values of v at concentration 0·005-normal, indicate the following order of the anions:

$$SO_4 > Cl > NO_3.$$

This order, which follows that of the well-known lyotropic series*, suggests also the order of adsorbability of the anions by the parchment-paper diaphragm. Such adsorption, which would tend to increase the initial negative charge of the diaphragm†, would be consistent with the charging effect indicated by the (e, concentration) curves relating to the cellulose and powdered-glass diaphragms. The series holds although the concentrations are expressed in gram-equivalents. The effect of the SO_4'' ion in producing initial increase in the value of v, as compared with the respective and approximately equal effects of the Cl' and NO_3' ions, the common ion in each case being Cu'', thus appears to be greater than would be explained by the influence of valency alone.

The electrolytic water-transport. H. Remy‡ and J. Baborovsky§, in the light of experimental evidence obtained with a considerable number of solutions, have concluded that the electro-endosmotic effect of a parchment-paper diaphragm may be neglected in the case of solutions of normal concentration. The liquid-transport obtained with normal cupric-chloride solution would thus be attributable wholly to electrolytic transference, i.e. v_f, table 1, would represent the electrolytic water-transport. The values of v_f over the concentration range 1·0-normal to 0·1-normal lie on a smooth curve, figure 3, the direction of liquid flow over this range of concentrations being opposite to that relating to concentrations 0·05-normal and less. The values of v_f for the latter series of concentrations also plot into a smooth curve, which appears, however, to be entirely unconnected with the continuation of the curve of figure 3. It seems evident from figure 2 that the electro-endosmotic effect of the parchment-paper diaphragm is considerably less pronounced with cupric-chloride solutions than with copper-sulphate solutions, and in the latter case the evidence adduced by the author in a former paper[*] suggests that the effect referred to becomes negligible at a concentration slightly greater than 0·2-normal. It therefore appears probable that the curve of figure 3, representing v_f for cupric-chloride solutions of concentrations normal to 0·1-normal, may be accepted as giving an approximate indication of the electrolytic water-transport over this range of concentrations.

---

* See H. Freundlich, *Colloid and Capillary Chemistry*, pp. 57, 58 (1926).

† The direction of electro-endosmotic flow, i.e. from anode to cathode, indicates that the diaphragm is negatively charged.

‡ *Trans. Far. Soc.* **23**, 383–385 (1927). See also H. C. Hepburn, *Proc. Phys. Soc.* **43**, 531–532 (1931).

§ *Z. Phys. Chem.* **129**, 129 (1927); *Coll. Czech. Chem. Comm.* **1**, 315 (1929).

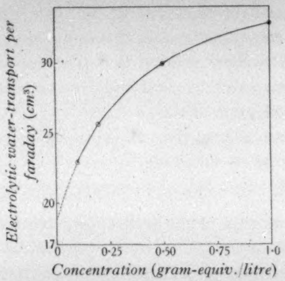


Figure 3. Electrolytic water-transport with solutions of cupric chloride.

Following the above, the reversal of liquid flow obtained with solutions of cupric chloride (i.e. a chloride of a bivalent cation) would be attributed to the effect of the electrolytic water-transport. In this connexion it is significant that the direction of liquid flow after reversal, i.e. from cathode to anode, is the same as that found by H. Remy and E. Manegold[†] for all cases examined of normal solutions of chlorides of bivalent cations[‡]; on the other hand, the direction of liquid flow found for the cases of normal solutions of chlorides of univalent cations was from anode to cathode. The result appears to be due mainly to the greater proportion of Cl' ions to cations in the case of solutions with bivalent cations, thus resulting in a preponderating electrolytic water-transport towards the anode in the latter case.

The values obtained by Remy and Manegold[§] for the electrolytic water-transport x (mol/faraday) in the case of normal solutions of magnesium chloride, calcium chloride, strontium chloride and barium chloride (all chlorides of bivalent cations), viz. 0·08, 0·20, 0·97 and 1·23 respectively, are somewhat lower than the value 1·82[||] obtained by the author for normal cupric-chloride solution.

§ 4. ACKNOWLEDGMENT

The author desires to thank Prof. A. Griffiths for facilities provided and for the interest he has shown in this investigation.

---

[*] *Proc. Phys. Soc.* **43**, 534 (1931).

[†] *Z. Phys. Chem.* **118**, 161 (1925).

[‡] See H. Remy, *Trans. Far. Soc.* **23**, 382 (1927).

[§] *Loc. cit.*

[||] $x = v_f/18{\cdot}02$, $v_f = 32{\cdot}8$, table 1.

621.317.738

A NEW CAPACITY-METER

By W. L. BECK, A.M.I.E.E.

Received July 24, 1933.

ABSTRACT. A new form of capacity-meter is described which simplifies the comparison of capacities over a wide range of values.

§ 1. THE RECTIFIER METHOD

The measurement of capacity in the new meter is based on the comparison of the impedance of the condenser under test with a calibrated standard impedance in a differential rectifier circuit described below, the balance being indicated by a d.-c. galvanometer.

In the circuit shown in figure 1 an unknown condenser C_1 and a standard condenser C_2 are each connected in series with a rectifier of bridge type, and placed in parallel on the same a.-c. supply. It can readily be seen that in this circuit there will be no deflection of the differential galvanometer G by the d.-c. currents of the rectifier bridges when the impedance of C_1 is equal to that of C_2. This assumes that the two rectifiers are of equal efficiency, and that the leakage currents through the condensers are negligible in comparison with their displacement currents, an assumption which may usually be made.

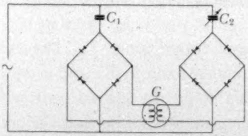


Figure 1.

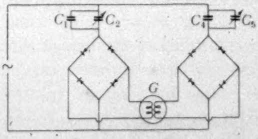


Figure 2.

The high sensitivity obtained with a d.-c. galvanometer renders this type of bridge valuable for the comparison of air-dielectric condensers. The effect of leakage and inequality of the two rectifiers may be eliminated by the use of the substitution arrangement shown in figure 2.

By a modification of the circuit it is possible to dispense with the differential galvanometer. One method is to connect the d.-c. circuits of the bridge rectifiers in direct opposition through a suitable galvanometer. With this arrangement, however, it is necessary to connect a resistance in shunt across each rectifier to protect it from damage. A more sensitive arrangement is shown in figure 3. In this circuit each bridge rectifier is replaced by two series—connected rectifier elements, and the double-wave rectifiers thus formed are connected in opposition through a simple moving-coil galvanometer. The a.-c. lead from each corner of the bridge is connected through a stopping condenser C_s to eliminate the short-circuit across the galvanometer.

§ 2. THE RECTIFIER CAPACITY-METER

A variable plate condenser with air dielectric forms a convenient continuously adjustable standard of capacity for this bridge. Its range, however, is limited to capacities of the order of a few hundred $\mu\mu$F. This difficulty has been overcome in the capacity-meter by connecting the condenser under test to the rectifier bridge through a multi-ratio single-wound current-transformer, in order to provide a number of ranges of capacity.

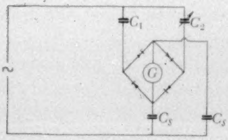


Figure 3.

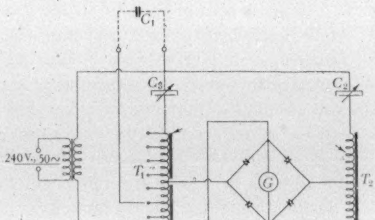


Figure 4.

The schematic circuit diagram of the instrument is shown in figure 4. The rectifier bridge is used in the same form as in figure 3 and the capacity C_1 under test is connected to the bridge through the tapped transformer T_1. The standard condenser C_2 has a maximum capacity of approximately 1200 $\mu\mu$F., and is connected to the bridge by a second transformer T_2. This steps up the current which is applied to the rectifier bridge in the ratio of approximately 3 : 1 so that the rectifiers work over a better part of their characteristic; this arrangement gives increased sensitivity and reduces the temperature coefficient of the rectifiers. To equalize the circuit, T_1 is connected to the bridge from a tapping which provides a similar ratio.

A small variable condenser C_3 is connected between the end of T_1 and the supply, to provide a convenient means of balancing the minimum capacity of C_2, and allows the capacity scale to be calibrated down to zero. This condenser also forms a convenient means of compensating for the capacity of the leads connecting the meter to the capacity under test. Thus if a preliminary balance is made by adjusting C_3 with one of the leads disconnected close to the test condenser, while the index of C_2 is on the zero of the scale, the capacity of the leads will be eliminated from any subsequent measurement.

The meter is fed from the supply mains by an insulating transformer which steps down the voltage across the condenser under test to approximately 100. A number of protective resistances which are not shown in figure 4 are introduced into the supply circuit by a switch mechanically coupled to the range switch, which selects the tapping on the transformer T_1. These protect the instrument from damage in the event of the leads to C_1 being short circuited.

The instrument as manufactured has a scale approximately 300 mm. in length, and is calibrated from zero to 1·2 μF. Eight ranges are provided having multiplying factors of 0·001, 0·005, 0·01, 0·05, 0·1, 0·5, 1 and 2. Thus it is possible to cover a range of capacities from 5 $\mu\mu$F. to 2·4 μF. Balance is indicated by a convenient self-contained d.-c. pointer galvanometer, which also indicates the direction of the out of balance capacity. The sensitivity is sufficient to show a departure from balance of one part in 1000 when the instrument is working over the upper part of the calibrated scale. The meter is normally arranged for an a.-c. supply voltage of 240 volts at 50 cycles per second, and its calibration is not changed by more than 0·3 per cent by a change in voltage of 25 per cent. In its present form, the calibration is accurate to at least 0·5 per cent of full scale reading, or 1 per cent of any reading above 0·2 on the scale.

The operation of the meter is extremely simple, and the use of a pointer moving over the calibrated scale renders the instrument particularly suitable for use under industrial conditions. For repetition work, maximum and minimum limits can readily be marked on the scale, making it unnecessary for the operator to read the actual value of the capacity.

The range of capacities on this model have been chosen to cover the normal requirements of industry. It is possible, however, to construct other models having ranges above or below these values. Thus, for instance, a special instrument could be arranged to give full scale for 100 $\mu\mu$F., or the upper end of the range could be extended to 12 or 24 μF.

§ 3. ACKNOWLEDGMENT

The instrument is being manufactured by the Cambridge Instrument Company Ltd., to whom the writer is indebted for permission to publish this paper.

546.212 : 548.7

THE MOLECULAR STRUCTURE OF ICE AND LIQUID WATER

By E. L. KINSEY and O. L. SPONSLER, University of
California at Los Angeles

Communicated by Sir William Bragg, F.R.S., July 25, 1933

ABSTRACT. In §§ 1 to 6 a lattice, new so far as the hydrogen-ion positions are concerned, and based on the oxygen positions previously determined by Barnes, is proposed for ice. The structure contains the units H^+ and $H^-_3O_2$, the latter built so that three hydrogen ions lie at the corners of an equilateral triangle in the plane midway between, and perpendicular to, the line of centres of the two oxygen ions. It consists of neutral chains extending parallel to the c axis and arranged about one another in a manner consistent with the symmetry and oxygen-position requirements. Large polarization effects arise, and reasons are given why a lattice in which they are produced is preferred to a co-ordination structure in which they are absent. The structure provides dihydrol as the polymer occurring in both ice and water, evidence for whose existence has arisen from various sources; and by means of a reasonable postulate in regard to the stability of the $H^-_3O_2$ ion in the crystal, and in clusters of dihydrol occurring in the liquid, it allows a qualitative explanation to be given of many of the abnormal properties of water and ice.

In § 7 the model is used to calculate the angle θ between the c axis and the line joining an oxygen with a hydrogen ion in the $H^-_3O_2$ unit, both when the unit is within the lattice and when it is within dihydrol regarded as isolated. The calculations are not exact, but indicate that $\theta = 30°$ to within a few degrees when the unit is in the lattice. The effect of the lattice on θ is shown to be small (several degrees), whereas the effect on the polarization of the oxygen is large and is such as to increase it nearly threefold over its value for isolated dihydrol. Use is made of this fact in accounting for the stability of dihydrol in the crystal lattice.

§ 1. INTRODUCTION

The abnormal properties of ice and water have received the attention of various workers for many years*. Many of the anomalies such as the abnormal temperature variation of the specific heat of the liquid, the lowering of the freezing-point with pressure, and the existence of a point of maximum density, have been explained by the hypothesis which supposes the liquid to be a mixture of simple H_2O molecules and polymers of these, a mixture that freezes into a solid in which the highest polymers appear as units. In order to explain the facts for the liquid the polymers have been assumed to be in temperature equilibrium with the simple molecules, to occupy more space than their constituent simple parts separately, and to require the addition of energy to dissociate them. Their existence has also been regarded, until fairly recently†, as affording a reason why water fails to obey many of the empirical relations connecting molecular weights with boiling-points, freezing-points and surface tension, relations which are obeyed by the so-called normal liquids.

---

* See H. M. Chadwell, *Chem. Rev.* **4**, 375 (1927) for review of the literature and bibliography.

† G. G. Longinescu, *Chem. Rev.* **6**, 381 (1929).

Recent spectroscopic studies of liquid water have offered evidence for the existence of polymers of a different nature. The discovery through the Raman effect of bands which vanish with increasing temperature and with the addition of an acid*, the occurrence of infra-red absorption bands in the liquid and solid states which are absent in the vapour†, and the abnormal shifts of other bands which occur upon the addition of an acid‡ offer significant support for existence of aggregates, aggregates which may be called molecules in the strictest sense. To this evidence should be added the results of X-ray diffraction studies in liquid water§, although their complete interpretation is not yet clear.

Suggestions have been made from time to time in regard to the nature of the polymers, but nothing definite seems to be known. For the liquid, mono-, di- and tri-hydrol have been assumed to exist, but any direct evidence for these assumptions has been lacking. For ice a suggestion has been made that it is composed of trihydrol, but so far no critical examination of the available X-ray data has been carried out to see whether such a unit can exist. In fact, the only lattice which has been proposed for ice as yet is ionic in character and does not contain a complex unit of any sort.

It is the purpose of this paper to show that on the basis of the present X-ray data on the crystal structure of ice a new lattice can be proposed which will account for the existence of a polymer, and which with the use of a reasonable postulate in regard to stability will also account, qualitatively, for many of the abnormal properties of both ice and water.

§ 2. THE BARNES LATTICE

The lattice positions of the diffracting centres in ice under normal conditions have been determined by Barnes‖ in such a thorough piece of work that there can be no doubt that the lattice given by him is correct, so far as the positions of the oxygen ions are concerned. Reasons are given by him for supposing the centres to be oxygen ions, and they are so considered here. The oxygen lattice has the hexagonal or trigonal symmetry of the space groups D_{6h}^4 or D_{3h}^4. There are four oxygens in a unit cell; each has a trigonal axis through it parallel to the singular axis, and each is at the centre of a tetrahedron whose corners are formed by other oxygen ions. The black spheres in figures 1 and 2 represent such a lattice. If a linear chain of these parallel to the *c* axis is examined, it will be seen to consist of ions spaced by alternate long and short intervals.

---

* E. H. L. Meyer, *Phys. Z.* **30**, 170 (1929); E. L. Kinsey, *Phys. Rev.* **35**, 284 (1930).

† J. W. Ellis, *Phys. Rev.* **38**, 693 (1931).

‡ E. L. Kinsey and J. W. Ellis, *Phys. Rev.* **36**, 603 (1930).

§ G. W. Stewart, *Phys. Rev.* **37**, 9 (1931); H. H. Meyer, *Ann. d. Phys.* **5**, **6**, 701 (1930).

‖ W. H. Barnes, *Proc. R.S.* A, **125**, 670 (1929).

The X-ray data furnished no information in regard to the positions of the hydrogens, and therefore Barnes was forced to assume positions for them which not only preserved the symmetry of the lattice but appeared reasonable. The lattice selected was a co-ordination one in which a hydrogen ion was placed at the mid point of each line joining a central oxygen ion with one at the corners of the surrounding tetrahedron. This choice brings one hydrogen ion into the middle of the short interval between oxygen ions along the *c* axis. An alternative arrangement which had to be considered, since the X-ray analysis failed to distinguish between the space groups D_{6h}^4 and D_{3h}^4, was obtained by rotating the three hydrogen ions lying in the basal planes about the *c* axis, so that they moved off the lines joining the two adjacent oxygen ions. But Barnes considered the first arrangement to be the more probable.

§ 3. OBJECTIONS TO A PURE CO-ORDINATION LATTICE

There appear to be various objections to a lattice of the type just described. In the first place, so far as we know, substances known to have a co-ordination lattice, and whose liquids have been studied, form electrically-conducting liquids. The alkali halides are typical examples. On the other hand, the crystal structures of substances which form non-conducting liquids seem to be of the non-coordination type. It therefore does not appear likely that a non-conducting liquid such as water will freeze into a pure co-ordination lattice in which the units are ions that are extremely difficult to separate.

In the second place, the melting-points of substances having co-ordination lattices are high, in most cases hundreds of degrees higher than the melting-point of ice. It is true that those for the halogen hydrides are low, but these substances in many respects are quite different from the salt-like bodies which possess co-ordination lattices. They are known to be poor conductors as liquids, and, for the reasons being set forth for water, they too may not possess co-ordination lattices.

In the third place considerations arise which lead one to suspect that a lattice will be formed in which there will be strong polarization. Hund*, in a discussion of the cadmium-iodide type of lattice (layer lattice) in which the iodine ion is strongly polarized because it is unsymmetrically surrounded by cadmium ions, sets forth the conditions which favour the existence of polarization. He shows that for the cadmium-iodide type the lattice energy is larger for the layer lattice than for a co-ordination structure, and that the energy increases with the ratio α/r^3, where α is the polarizability and r is the ionic distance. Thus, layer lattices are more stable energetically than co-ordination ones in cases where α is large and r is small. In the ice lattice, for reasonable positions of the hydrogen ions, the oxygen-oxygen distances require very small oxygen-hydrogen distances. In the Barnes lattice, for example, if the oxygen-ion radius is taken as 1·32 Å.†, that for the hydrogen ion becomes 0·08 Å., and if the value 1·40 Å. of Pauling‡ is taken, no room at all is left for the proton. Such a close approach of two ions is not known for any lattice yet examined, so far as the authors know. The lithium cation is next smallest with a radius of 0·8 Å. It is evident that the slightest departure from a co-ordination arrangement, where such small distances are involved, will result in strong polarizing fields. In addition, the oxygen ion itself has a substantial polarizability, so that the two conditions necessary for the formation of some type of "layer or chain" lattice are certainly present.

---

* F. Hund, *Z. f. Phys.* **34**, 833 (1925).

† See V. M. Goldschmidt, *Trans. Faraday Soc.* **25**, 253 (1929).

‡ L. Pauling, *Proc. R.S.* A, **114**, 181 (1927).

In the fourth place, a consideration of the series Ag_2O, Cu_2O, Li_2O, H_2O shows that the large difference in properties between the first three and water will require some fundamental change in the type of lattice. The first three have cubic co-ordination lattices. Table 1* indicates the extent of the dissimilarity expected.

Table 1

	Radius ratio	Radius sum
Ag_2O	0·855	2·45
Cu_2O	0·727	2·28
Li_2O	0·591	2·16
H_2O (Barnes's lattice)	0·061	1·40

Through suggestions of this sort we have been led to look for a lattice more like the layer type than the co-ordination type, i.e. for one in which strong polarization can occur.

§ 4. THE PROPOSED NEW ICE LATTICE

A consideration of Barnes's oxygen lattice will show that another arrangement of hydrogen ions, different from any of those mentioned by him, is possible. If the hydrogen ions are placed in the symmetry plane which passes midway between the oxygen ions and is perpendicular to the *c* axis, in such a way that three of them form an equilateral triangle whose centre lies at the mid point of the short oxygen-interval and upon one of the *c* axis chains, and a fourth, to be designated as the "singular hydrogen ion," is placed on the *c* axis chain at the mid point of the long oxygen-interval, all of the symmetry requirements of the lattice are still obeyed, and the proper number of hydrogen ions is provided. Figures 1 and 2 represent a model built in this way, in which the black and white spheres represent oxygen and hydrogen ions respectively. The three hydrogen ions which form triangles in the basal planes will be referred to as type *T* hydrogen ions. Planes of symmetry parallel to the basal plane and trigonal axes parallel to the *c* axis are still preserved. Equally spaced basal planes may be drawn such that every alternate one contains hydrogen ions, and the others locate two oxygen planes close together, as can be seen in figure 2.

A more significant view is provided by considering a chain of oxygen ions parallel to the *c* axis. If the double-pyramidal group H_3O_2 is regarded as a unit, any one chain is seen to be a column of such groups and H^+ ions alternately spaced. Moreover if the group $H^-{}_3O_2 . H^+$ is regarded as a dipole it is seen to be surrounded laterally by three others pointing oppositely, while along the *c* axis the dipoles are strung end to end. The whole lattice may be described as a cluster of linear chains of dipole dihydrol units. But it is not safe to carry this view too far, for it is obvious that because of its symmetrical position half way between two $H^-{}_3O_2$ groups, a singular hydrogen ion cannot be associated definitely with any one of them, at least in the lattice at equilibrium. However, in what follows, it will be convenient on occasion to regard the dihydrol group $(H^+.H^-{}_3O_2)$ as a unit whose properties may be examined.

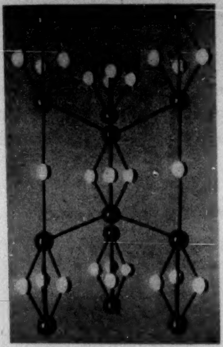


Figure 1 *A*.

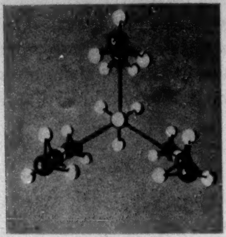


Figure 1 *B*.

Figure 1. Four *c* axis chains of proposed ice lattice. *A*, view of model perpendicular to *c* axis; *B*, view of model along *c* axis. White and black spheres represent centres of hydrogen and oxygen ions respectively.

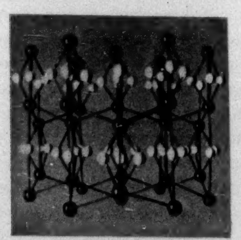


Figure 2 *A*.

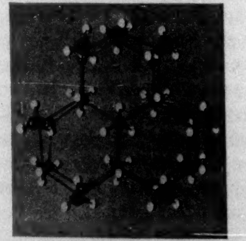


Figure 2 *B*.

Figure 2. Extended model of ice lattice. *A*, basal planes; *B*, hexagonal structure.

It is evident that because of the unsymmetrical environment of hydrogens the oxygen ions are now in electric fields directed along the *c* axis toward the singular hydrogen, and that polarization of the ions in this direction will result.

§ 5. POSTULATE OF A LIMIT OF STABLE APPROACH FOR THE SINGULAR HYDROGEN

It is not possible to fix through symmetry restrictions alone either the orientation of the triangle of three hydrogens or its size, but through certain assumptions in regard to the crystal forces involved some idea of the order of magnitude of the angle θ between the c axis and the line from an oxygen to a hydrogen of the triangle, as well as of the orientation of the triangle, may be obtained. These considerations are given in § 7. They show that an angle within a few degrees of 30° is reasonable. They also show that the orientation of the triangle given in figure 1 *A* is probably the stable one. If these results are assumed, the oxygen-singular-hydrogen distance of 2·32 Å. is about 1·4 times the oxygen-T-hydrogen distance of 1·61 Å. If the T hydrogens are regarded as spheres resting upon the surface of an oxygen ion of radius 1·40 Å. (or 1·32 Å.), the radius of the hydrogen ion becomes about 0·21 Å. (or 0·29 Å.). The singular hydrogen ion is then not in contact with an oxygen ion, but is held in equilibrium away from it by electrostatic forces which are due partly to the ionic charges of the $H^{-}_{3}O_{2}$ group and partly to the polarization of the surrounding oxygen ions. The interval between the surfaces of the two ions is 0·71 Å. When the dihydrol unit is removed from the lattice these forces of repulsion become smaller*, for the effect of the neighbouring ions is to increase the oxygen polarization and hence to increase these repulsive forces. If they are weakened the singular hydrogen will approach the $H^{-}_{3}O_{2}$ group. The absence of evidence for the existence of dihydrol in the vapour state indicates that its stability in the solid and liquid depends upon a repulsive force sufficient to maintain a minimum singular-hydrogen-H_3O_2 distance of approach. We have been led, therefore, to make the following postulate. *A critical distance of approach between the singular hydrogen and* H_3O_2 *groups exists such that when the approach is smaller, the dihydrol unit is unstable and spontaneously dissociates into two simple* H_2O *molecules.* Stability of the unit in the crystal is produced by increased polarization forces which result from the fields of the surrounding ions; and these fields maintain the singular hydrogen at distances from the $H^{-}_{3}O_{2}$ group larger than the critical distance of approach. Electric fields are present in liquid water also, so that if the same unit exists there (and from the optical evidence it is reasonable to suppose that it does†) its stability is maintained by large polarization in the same way.

The ability of the postulate to provide those properties for polymers which it has always been necessary to assume in order to account qualitatively for some of the abnormalities of water is immediately evident. It will be of interest to consider briefly some of these abnormalities.

---

* Cf. § 7.

† J. W. Ellis, *Phys. Rev.* **38**, 693 (1931).

§6. SOME PROPERTIES OF ICE AND WATER FROM THE POINT OF VIEW OF THE PROPOSED LATTICE

Since the lattice is rendered unstable by any factors which cause too close an approach of the units along the *c* axis, increased pressure should produce a lowering of the lattice melting-point. Thus, the lattice provides for this well-known property of ice. Melting may be regarded as a destruction of the lattice due, primarily, to too close an approach of the singular hydrogen and H_3O_2 groups, resulting in a liquid which is a mixture of mono- and di-hydrol in temperature equilibrium.

The occurrence of a point of maximum density may be explained in the usual way. As the temperature rises from 0° an increase in dissociation of the more voluminous dihydrols into the more compact monohydrols will arise superposed upon a decrease in density caused by the increased temperature motion. These opposing effects will result in a point of maximum density which, according to the model, should shift to lower temperatures as the pressure is increased. This shift is another well-known behaviour of liquid water*.

The increase in compressibility of ice, which within certain limits occurs instead of the usual decrease as the pressure is increased*, can also be accounted for. Under those pressures for which the dihydrol lattice is stable, closer approach of the units along the *c* axis weakens the crystal repulsive forces, since unstable positions are being approached. The form of the potential-energy curve postulated for the dihydrol group, regarded as a diatomic molecule in the crystal lattice, serves to show this effect, figure 3. The compressibility is large in the regions near the limits of stability.

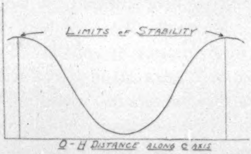


Figure 3.

Under sufficiently high pressures the lattice should disintegrate whatever the temperature. That ice behaves in this way is well known from Bridgman's work*. But the phenomena are not simple, as is shown by the existence of the many different modifications of ice. What is significant is that at the highest pressures all the properties of ice become normal, a point which Bridgman has emphasized. From the present point of view we may regard this as due to a transformation by stages from the dihydrol chain type of lattice to one completely regular in its behaviour, perhaps to one of co-ordination type such as Barnes suggested.

It should be mentioned also that the existence of a minimum in the specific-heat curve for water, and its displacement by pressure to lower temperatures, are accounted for in Nernst's usual way, since the dihydrol discussed here requires energy to dissociate it in the lattice.

---

* P. W. Bridgman, *Proc. Am. Acad. Arts and Sci.* **47**, 441 (1911–12).

There are other properties which it is profitable to consider from this point of view, but since they have to do with absorption and Raman scattering in water and acid mixtures they will be discussed elsewhere.

§ 7. CALCULATIONS

To obtain some idea of the probable equilibrium configuration of the H_3O_2 anion in the crystal lattice, it is convenient to treat the group as isolated, and then to determine the modifications which arise when it is introduced into the lattice. Three types of field are recognized as being effective, namely electrostatic fields due to the ionic charges, polarization fields due to the polarization of the oxygen ions, and repulsive fields, regarded as non-electrical, acting between the hydrogen ions and oxygen ions. For simplicity the calculation will at first involve only the ionic and repulsive forces between oxygen and hydrogen ions. A second calculation will take into account the polarization forces together with the effect of the lattice.

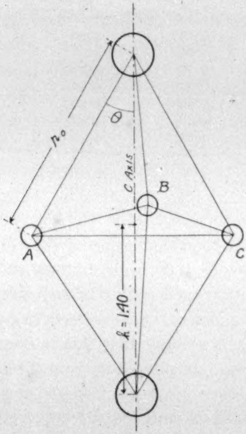


Figure 4. $H^-{}_3O_2$ unit. Large circles represent oxygen ions, small circles hydrogen ions.

Calculation of the angle θ for the isolated $H^-{}_3O_2$ *ion*. Since at equilibrium the forces in the plane of the triangle *ABC*, figure 4, on any one hydrogen ion and directed toward the *c* axis vanish,

$$\frac{4e^2}{r_0^{\,2}}\sin\theta - F(r_0)\sin\theta - \frac{e^2}{2h^2\tan^2\theta\cos 30^\circ} = 0 \qquad \ldots\ldots(1),$$

where *e* is the electronic charge, $F(r_0)$ is the value of the repulsive force between hydrogen and oxygen ions at equilibrium, and the other symbols are as represented in the figure.

e, $F(r_0)$
h, θ

Similarly, the forces along the *c* axis on an oxygen ion and directed toward the centre of the H_3O_2 group must vanish at equilibrium, giving

$$\frac{6e^2}{r_0{}^2}\cos\theta - \frac{e^2}{h^2} - 3F(r_0)\cos\theta = 0 \qquad \text{......(2).}$$

From equations (1) and (2) a single equation for θ can be obtained:

$$6x^3 + 1 = \frac{\sqrt{3}\,x^3}{(1 - x^2)^{3/2}} \qquad \text{......(3),}$$

where $x = \cos\theta$. This may be solved by calculating the quantities

$$y_1 = \frac{\sqrt{3}\,x^3}{(1 - x^2)^{3/2}} \quad \text{and} \quad y_2 = (6x^3 + 1),$$

and setting $y_1 = y_2$. From table 2, the solution is seen to be $\theta = 37°$.

Table 2

θ	y_1	y_2	$y_2 - y_1$
30°	9·16	4·90	− 4·54
31	8·00	4·78	− 3·22
32	7·17	4·66	− 2·51
33	6·31	4·54	− 1·86
34	5·64	4·42	− 1·22
35	4·98	4·30	− 0·68
36	4·51	4·18	− 0·33
37	4·06	4·06	0·00
40	2·98	3·70	+ 0·72
50	1·03	3·29	+ 2·26

Effect of the lattice and the polarization forces. For the calculations which follow it is necessary to choose an orientation about the *c* axis for the triangle of three hydrogen ions. It has been assumed such that any side of the triangle is opposite one of the three surrounding chains, i.e., the vertices point symmetrically between any two of these chains. It is evident that this is one of two positions in which the torque on the H_3O_2 group, considered as a rigid body, is zero. A 60° rotation about the *c* axis gives the other position. Considering the effects of only the six immediately surrounding oxygens and the three surrounding singular hydrogens, it can be shown that the first position is stable and the second unstable. The calculation is the elementary one of considering the derivative of the torque in respect to the angle of orientation. Polarization fields have been neglected, so that the value of this result lies principally in indicating that the orientation used is the more likely of the two, for contributions to the torque due to polarization may be expected to be small.

c_1 c_2

The effect of the lattice and the polarization fields will be represented by two terms; c_1e^2, the force on a hydrogen of the triangular group, in the plane of the triangle and directed away from its centre; and c_2e^2, the force on an oxygen ion parallel to the *c* axis and directed away from the centre of the $H^{-}{}_3O_2$ group. These must be subtracted from the left-hand sides of equations (1) and (2) respectively, which become

$$\frac{4e^2}{h^2}\cos^2\theta\sin\theta - F(r_0)\sin\theta - \frac{e^2}{2h^2\tan^2\theta\cos 30^\circ} - c_1e^2 = 0 \quad \text{......(4)},$$

$$\frac{6e^2}{h^2}\cos^3\theta - \frac{e^2}{h^2} - 3F(r_0)\cos\theta - c_2e^2 = 0 \quad \text{......(5)}.$$

In these equations r_0 has been replaced by $h/\cos\theta$. As before, a single equation may be obtained:

$$6x^3 + 1 = \frac{\sqrt{3}\,x^3}{(1-x^2)^{3/2}} + g \quad \text{......(6)},$$

where $g = h^2(3c_1\cos\theta - c_2)$ ......(7). g

The solution is that value of x which satisfies

$$y_2 - y_1 = g \quad \text{......(8)}.$$

The terms c_1 and c_2 contain (1) charge and polarization effects of the lattice, and (2) polarization effects of the $H^-{}_3O_2$ unit itself. So far as the angle θ is concerned the lattice effect is small (as is seen in what follows), so that its variation with θ has been disregarded. It has been calculated for a fixed angle of 36°. For the polarization effects in the unit, however, variations in θ become important. The terms are therefore functions of θ and are obtained for a series of θ values by calculating the inverse-square fields at an oxygen and a hydrogen of the triangle due to the surrounding charges and to the oxygen dipoles of polarizability α. The calculation is only approximate but has considered, in addition to the effect of a group's own chain, the effect of the first three and the next six surrounding chains. The smallness of this correction makes it of little value to extend the calculation further. Similar ions are arranged into sets, and the effect of each set is expressed by a series whose terms grow rapidly smaller. The effects neglected are of the order of a few per cent of the terms used.

For a field F at an oxygen dipole the terms become F

$$c_1 = 0{\cdot}0088 - (0{\cdot}0491 - M)\,\alpha F \quad \text{......(9)},$$

$$c_2 = 0{\cdot}091 + (0{\cdot}0234 - N_1)\,\alpha F + 0{\cdot}158\,\alpha^2F^2 \quad \text{......(10)},$$

where $M = 2{\cdot}90\sin\theta\cos^4\theta$, $N_1 = 1{\cdot}45(3\cos^2\theta - 1)\cos^3\theta$, and these terms represent the effect on a hydrogen ion of the polarization forces arising within the unit, and the effect of the triangle of three hydrogens on an oxygen dipole, respectively. The field F is given by M, N_1

$$F = K - 0{\cdot}255 - 0{\cdot}0507\,\alpha F \quad \text{......(11)},$$

where $K = 1{\cdot}53\cos^3\theta$ and represents the effect of the triangle of three hydrogens. K

Values for these quantities are obtained by using Pauling's calculated value of the mol refraction, $R = 9{\cdot}88$, for the oxygen ion*. Since the polarizabilities of many ions in crystals have been found to be less than the values calculated for the free ions, we may regard this as an upper limit for α†.

---

* L. Pauling, *Proc. R.S.* A, **114**, 181 (1927).

† H. Heckman, *Z. f. Phys.* **31**, 219 (1925).

From the relation $R = \frac{4}{3}\pi N\alpha$, where N is Avogadro's number, the value

$$\alpha = 3{\cdot}9 \times 10^{-24}\ \text{cm}^3$$

is obtained. For convenience α is expressed in units of 10^{-24} cm^3, and the field F in units of 10^{16} e.s.u. These are the units used in equations (9), (10) and (11). Table 3 gives the values of the quantities c_1, c_2, g, $(y_2 - y_1)$, and F as functions of θ. c_1 and c_2 are expressed in units of 10^{16}.

Table 3

θ	c_1	c_2	g	$(y_2 - y_1)$	F
27°	—	—	—	−7·85	—
28	−2·03	−2·35	−5·97	−6·34	0·67
29	−1·95	−2·12	−5·86	−5·18	0·65
30	−1·84	−1·87	−5·72	−4·54	0·62
31	−1·83	−1·64	−5·97	−3·22	0·59

Columns four and five show that for g to be equal to $(y_2 - y_1)$, which is the condition for equilibrium, θ must be, approximately, 28°.

The reduction from 37°, the angle for the isolated group, is due to the effect of the lattice and to the oxygen polarization. Since it is of interest to separate these two effects, calculations for θ, which include in every case the polarization effects, have been made for the following cases: (1) the $H^-{}_3O_2$ group isolated, (2) the group $H^-{}_3O_2$ on its chain and surrounded by three neighbouring chains, (3) the group on its chain surrounded by the first three and the next six chains, and (4) the group $(H_2O)_2$ isolated. The results are shown in table 4.

Table 4

	θ	F
$H^-{}_3O_2$ isolated	28°	0·54
$H^-{}_3O_2$ + 3 chains	27	0·78
$H^-{}_3O_2$ + 3 + 6 chains	28	0·67
$(H_2O)_2$ isolated	31	0·24

By comparison of the first three rows of the table, the effect of the lattice on θ is seen to be negligible. The polarizing field F, however, exhibits a greater variation. Rows three and four show that when the dihydrol group, $(H_2O)_2$, is in the lattice, the field F approaches nearly three times the value of the field when the group is isolated. Further, a simple calculation, using Pauling's value of the polarizability, shows that the small value of F for the isolated dihydrol is not sufficient to prevent the singular hydrogen ion from approaching and actually resting upon the surface of the oxygen ion. The model, therefore, is in accord with the view presented in previous sections, that the oxygen-singular-hydrogen separation is maintained only by forces which arise within the lattice.

The effect of a non-electrical repulsive force between the two oxygen ions so far has been omitted. Since they are in contact if Pauling's value for the oxygen ion radius is assumed, it is reasonable to suppose that such a force exists. If it does, it will affect the term c_2 only, and in such a way as to make it larger; and since this term is always negative its absolute value will be smaller. This will make the absolute value of g larger, as a glance at equation (7) shows, and hence will decrease the angle θ below 28°.

We may conclude, therefore, that an upper limit of 37° for θ is reasonable, and that the angle is more likely to be nearer 30° than 37°.

§ 8. CONCLUSION

The foregoing remarks show that a lattice may be assumed for ice which accounts in a very reasonable way for the existence of a complex group in both the solid and the liquid states. The solid is regarded as a lattice of two types of ions, the H cation and the complex double pyramidal anion H_3O_2, which form neutral chains parallel to the c axis. At the melting-point, a temperature lower than that required to cause the ionic dissociation $H^+ . H^-{}_3O_2 \rightarrow H^+ + H^-{}_3O_2$, a re-arrangement of hydrogen ions, of such a character as to produce large numbers of single water molecules, occurs. These will exist in temperature equilibrium with the remaining dihydrol, which is prevented from dissociating by the fields that are still present in the liquid. It cannot be supposed, however, that the true state of the liquid is completely represented by so simple a picture. Clusters of variable size of the two types of molecules no doubt are the mobile units. In fact, the X-ray diffraction phenomena point to the existence of a kind of orderly clustering which may follow the crystalline arrangement. The significance of the view presented lies in the fact that a structure of ice can be assumed which is compatible with the X-ray data, admits of the existence of a polymer, and can provide for many of the abnormalities exhibited by the substance.

535·338:546.812

THE BAND SPECTRUM OF TIN OXIDE

BY F. C. CONNELLY, A.R.C.S., B.Sc., D.I.C.
Imperial College, South Kensington

Communicated by Prof. A. Fowler, F.R.S., July 14, 1933

ABSTRACT. The spectrum of SnO has been produced by a flame source which offers considerable advantages over the arc previously used by Mahanti, and the spectrum has also been obtained in absorption. Experimental evidence has been secured confirming that the emitting molecule is SnO. The vibrational analysis of Mahanti's *A* system has been extended to $v' = 8$, and approximate values of the vibrational constants have been calculated from the band-head data. The lower electronic level of this system has been shown to be the ground state. It is doubtful whether the so-called *B* and *C* systems actually exist as separate systems.

§ 1. INTRODUCTION

THE spectrum of tin oxide, SnO, consists of well-marked bands degraded to the red, and extends through the blue and near ultra-violet. The bands were observed by Eder and Valenta* in the oxy-coal-gas flame spectra of tin sulphide and tin chloride, and afterwards in the arc spectrum of metallic tin on carbon poles by Mahanti†. Mahanti measured the band heads on photographs of the tin arc in air, and arranged many of them in three systems which he designated *A*, *B* and *C*. The principal bands all fall into the *A* system, the *B* and *C* systems being only fragmentary.

The use of the arc, however, has the disadvantage that the accompanying line spectrum of tin and bands of CN and C_2 tend to obscure the oxide bands; and a further difficulty arises from the great extension of individual bands, due to the high temperature of the source, the tails of the stronger bands overlapping and covering the weaker heads.

The aim of the present investigation was to record the positions of the band heads as completely as possible by the use of a flame, and to extend the vibrational analysis of the spectrum.

§ 2. THE MOLECULE EMITTING THE SPECTRUM

Mahanti attributed the spectrum to the oxide molecule SnO, after eliminating the possibility of its being due to SnH or Sn_2. Analysis of the bands has shown that the molecule SnH must be ruled out, but some doubt was felt as to whether Sn_2 might not be the molecule concerned. Mahanti considered this improbable for two reasons: firstly, on account of the occurrence of the bands when tin salts were heated in the strongly oxidizing flame; and secondly because he saw no alternations of intensity in the lines of a given branch of those bands which he could observe under high dispersion. Such alternations would be visible if the molecule were symmetrical.

---

* *Atlas Typischer Spektren.*

† *Z. f. Phys.* **68**, 114 (1931).

In the present work, however, the source has been a reducing flame of hydrogen containing stannic-chloride vapour. This flame contains a considerable quantity of metallic tin vapour, which will readily condense on any cold body held in the flame. The first reason given by Mahanti therefore carries little weight, as the spectrum is obtainable from both oxidizing and reducing flames.

As regards the alternations of intensity, careful examination of the (1, 0) and (2, 0) bands does suggest some such alternations in lines of the same branch, but the dispersion in the first order of the 10-ft. grating is not sufficient to make it quite certain that the variations are not due to overlapping.

It was therefore considered desirable to obtain further experimental evidence with regard to the molecule emitting these bands. Accordingly an enclosed arc chamber was set up, in which an arc could be maintained in gases other than air, at either atmospheric pressure or reduced pressures. Owing to the low melting-point of tin, solid rods of the metal could not be used in the usual way. The lower pole was an iron cup 2½ cm. in diameter and containing the tin, which became molten when the arc was struck; while the upper pole was a hollow copper rod, cooled right up to the tip by running water. In operation, the copper became covered with a layer of tin condensed from the arc, so that copper lines were only faintly visible.

The characteristic bands were readily obtained when air was used in the arc chamber. After careful removal of all oxide from the poles, hydrogen was introduced into the chamber, but it was not found possible to obtain the bands in this gas although different pressures were used. Negative results were also obtained when nitrogen was used. It must therefore be considered extremely probable that SnO is the molecule concerned, since oxygen appears to be necessary for the production of the spectrum.

§ 3. THE LIGHT-SOURCE

The light-source first employed in the present work was a hydrogen flame burning in air at a silica jet. The hydrogen was taken from a cylinder and was passed through a Wolff's bottle containing anhydrous stannic chloride, $SnCl_4$. It was not necessary, or indeed desirable, actually to bubble the gas through the liquid, as a sufficient quantity of vapour became mixed with the hydrogen when this was simply passed over the surface of the liquid in the bottle.

The flame obtained in this way is bright blue in colour and has a faint yellow centre, presumably due to the emission of continuous radiation from heated particles of oxide in the solid state. In the outer parts of the flame the temperature is sufficiently high to vaporize the solid. In later experiments, made for the purpose of studying the absorption spectrum of the flame, nitrogen was mixed with the hydrogen to reduce the temperature, and it was then observed that the yellow central portion rose through the outer blue region and appeared above the rest of the flame. Photographs of the flames with hydrogen alone and with hydrogen-nitrogen mixture are shown at (*g*), (*h*) in the plate.

These flames have a peculiar appearance and it is probable that an examination of their structure would yield useful information on the chemical changes involved in flame reactions*.

The flame spectrum obtained in this way was notably free from superposed impurities, only a faint trace of the OH band at λ 3064 being visible on a strongly exposed plate. Lines of tin were entirely absent, but it is interesting to note, in view of the possibility of the bands being due to Sn_2, that the resonance lines of tin at λλ 2863·3 and 2840·0 appeared in the absorption spectrum of the same flame as described later. With spectrographs of moderate dispersion the exposures were not unduly long, half an hour being sufficient to obtain a strong plate on the Hilger E 2 quartz spectrograph.

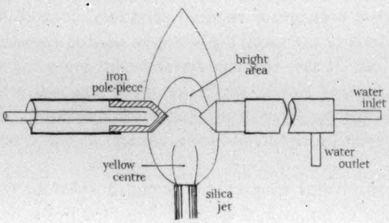


Figure 1.

The source was made very much brighter by passing a high-tension a.-c. arc through the flame, between water-cooled hollow iron pole-pieces about ½ to 1 cm. apart. The arc was fed by a transformer supplying about 0·2 ampere at 5000 volts. The increased luminosity was not confined to the region of the flame directly between the poles, but extended over a crescent-shaped area above them. With this arrangement, figure 1, exposure times were reduced to one-tenth of those required for the flame alone. The spectrum obtained from this arc flame was intermediate between that of the simple flame yielding short bands and that of the metal arc in air giving extended and overlapping bands. A few of the stronger iron lines which appeared in the spectrum could readily be distinguished by means of the iron comparison spectrum. The OH band was rather more strongly developed than in the normal flame, and as this tended to obscure some of the bands near λ 3200, the flame source was used without the high-tension arc for photographs in this region.

---

* When titanium chloride, a volatile fuming liquid, was used in place of stannic chloride, a flame of similar form was obtained. There were, however, no signs of titanium-oxide bands. They were either completely masked by the strong continuous spectrum from the white-hot particles of titanium oxide in the central region of the flame, or, as seems more probable, the temperature was not sufficiently high to vaporize or excite the oxide molecules. This view receives confirmation from the work of Dr A. S. King, *Publ. Astr. Soc. Pac.* **36**, 140 (1924), who found that in the electric furnace the TiO bands appeared only at temperatures above 1900° C.

§ 4. THE ABSORPTION SPECTRUM

It became evident, during the consideration of the various electronic levels involved in Mahanti's three systems of bands, that considerable assistance might be expected from an examination of the absorption spectrum. A beam of white light, obtained by burning magnesium ribbon in a holder with a clockwork feed, was passed through a flame of hydrogen containing stannic-chloride vapour as before. In order to give a longer path for absorption, the flame was wide and flat in shape. Metal screens were arranged on either side of the flame to ensure that all the light reaching the slit of the spectrograph had passed through the flame. The magnesium ribbon burnt in this way is a convenient source of continuous radiation in the near ultra-violet region. The absorption spectrum is shown at (*b*) in the plate.

§ 5. THE ACTIVE NITROGEN METHOD OF EXCITATION

The spectra of certain oxides, such as BO and SO, can be conveniently excited by active nitrogen which has not been completely freed from oxygen. Bands produced by active nitrogen are the short bands characteristic of a low-temperature source. Consequently an attempt was made to produce the SnO bands by this means, in order to compare them with those from the flame sources. A quantity of stannic chloride was enclosed in a glass bulb and the vapour was allowed to pass, under control of a tap, into a stream of active nitrogen in the manner adopted by Strutt and Fowler*.

As has been stated by these observers, a bright blue glow is produced where the streams of active nitrogen and tin-chloride vapour come into contact, and the spectrum is characterized by a group of closely spaced narrow bands extending from about λ 4000 to λ 4500. This spectrum is clearly quite different from that given by the flame. No heads can be detected and the contrast between dark and light portions is not very strong, so that it is difficult to observe the bands under large dispersions. Photographs taken on the Hilger E 1 quartz spectrograph do not show any of the structure usually associated with diatomic molecules. This system of bands is therefore apparently not connected with the SnO bands which have been obtained in the flame.

So far as is known these bands have not been investigated further since they were first described by Strutt and Fowler. The similarity in colour between the glow in active nitrogen and the flame makes confusion easy, but the spectra are quite different in character.

---

* *Proc. R.S.* A, **86**, 105 (1912).

§ 6. DETERMINATION OF WAVE-LENGTHS

Numerous photographs of the flame and high-tension arc in flame were obtained with Hilger E 1, E 2 and small quartz spectrographs, and in the first order of the 10-ft. concave grating of this laboratory. Measurements were made on several of the plates taken with the E 1, E 2 and grating instruments. The dispersions given by these instruments were as follows:

E 2 47 Å./mm. at λ 4300 to 18 Å./mm. at λ 3100,
E 1 16 Å./mm. at λ 4400 to 5 Å./mm. at λ 3100,

10-ft. concave grating 5·4 Å./mm. in the first order.

The larger dispersion on the grating plates did not always give correspondingly greater accuracy in the wave-length measurements of the bands, owing to the rather indefinite nature of the unresolved band lines forming the heads. To obtain the fine structure necessary for the determination of the origins of the bands, which are of greater importance than the heads from a theoretical point of view, would require much higher resolving-power than was available.

Panchromatic plates were used to explore the yellow and red parts of the spectrum, but as no bands were found there, Imperial Ordinary plates were used for the blue and ultra-violet. Measurements were made in the usual way with a Hilger photomicrometer, and the iron lines adopted as standards were, as far as possible, those recommended as secondary standards by the International Astronomical Union.

Particulars of the observed bands are included in table 1, which indicates wave-lengths in air, wave-numbers *in vacuo* and relative intensities of the band heads.

§ 7. VIBRATIONAL ANALYSIS

Mahanti classified the bands he observed into *A*, *B* and *C* systems. Most of the bands have been placed in the *A* system, the other systems being composed of fainter bands towards the less refrangible end.

Table 1 contains, in addition to the measurements, the values of v' and v'' assigned by the author in the empirical analysis of the vibrational structure. It also includes all the bands recorded by Mahanti and shows the system—*A*, *B* or *C*—in which each band was placed by him. It will be seen that during the present investigation a considerable number of bands have been observed which were not included in Mahanti's tables. When a band has been observed by Mahanti, but not found by the author, Mahanti's value of the wave-number is given in square brackets.

The principal bands of the spectrum, and numerous fainter ones, can be arranged in a Deslandres scheme as shown in table 2, v' taking values from 0 to 8 and v'' from 0 to 9.

The bands analysed by Mahanti are those having values of v' from 0 to 3 only. By means of the flame source previously described, the higher members of the v'

Table 1

λ (in air) and intensity	ν (in vacuo)	v', v''	Mahanti's classification
4660·9 (1)	21448		
4633·5 (1)	21576		
4612·4 (0)	21675		
4590·8 (0)	21777		
4569·5 (0)	21878		*C* (0, 3)
4540·9 (0)	22016		
4522·4 (0)	22106		
4498·7 (1)	22222		
4487·9 (0)	22276		*A* (1, 10)
4452·48 (1)	22453·1		*C* (1, 3)
4428·90 (2)	22572·6		
4411·40 (3)	22662·2		*C* (0, 2)
4388·47 (0)	22780·6		
	[22831·4]		*A* (2, 10)
4365·36 (0)	22901·2		*B* (0, 3)
	[23020·0]		*A* (1, 9), *C* (2, 3)
4302·87 (3)	23233·8		*C* (1, 2)
	[23194·7]		*A* (0, 8)
	[23380·7]		*A* (3, 10)
4262·30 (3)	23454·9		*C* (0, 1)
4240·34 (2)	23576·4	(2, 9)	*A* (2, 9)
4217·74 (3)	23702·7		*B* (0, 2)
4174·42 (0)	23948·7		*A* (0, 7)
4161·00 (1)	24025·9		*C* (1, 1)
4144·41 (1)	24122·1	(3, 9)	*A* (3, 9), *B* (2, 3)
4121·61 (2)	24255·5		*C* (0, 0)
4112·24 (2)	24310·7		*B* (1, 2)
4108·88 (2)	24330·7	(2, 8)	*A* (2, 8)
4079·14 (3)	24508·1		*B* (0, 1)
4068·2 (1)	24574		
4052·2 (1)	24671		
4025·83 (0)	24832·6		*C* (1, 0)
4019·35 (2)	24872·6	(3, 8)	*A* (3, 8)
3983·91 (3)	25093·9	(2, 7)	*A* (2, 7)
3978·72 (2)	25126·6		*B* (1, 1)
3950·97 (2)	25303·1	(1, 6)	*A* (1, 6)
3947·58 (1)	25324·8		*B* (0, 0)
3935·84 (1)	25400·3		*C* (2, 0)
3919·51 (1)	25506·2	(0, 5)	*A* (0, 5)
3899·31 (2)	25638·3	(3, 7)	*A* (3, 7)
	[25737·9]		*B* (2, 1)
3877·55 (0)	25782·2		

λ (in air) and intensity	ν (in vacuo)	v', v''	Mahanti's classification
3864·87 (3)	25866·8	(2, 6)	
3854·17 (0)	25938·6		*B* (1, 0)
3833·24 (2)	26080·2	(1, 5)	*A* (1, 5)
3802·70 (2)	26289·7	(0, 4)	*A* (0, 4)
3779·34 (1)	26452·1		
3752·30 (1)	26642·8	(2, 5)	*A* (2, 5)
3721·23 (3)	26865·2	(1, 4)	*A* (1, 4)
3691·39 (5)	27082·4	(0, 3)	*A* (0, 3)
3677·68 (0)	27183·3	(3, 5)	*A* (3, 5)
3644·6 (0)	27430	(2, 4)	*A* (2, 4)
3614·75 (3)	27656·6	(1, 3)	*A* (1, 3)
3585·40 (7)	27883·0	(0, 2)	*A* (0, 2)
3574·53 (0)	27967·7	(3, 4)	*A* (3, 4)
3542·39 (1)	28221·5	(2, 3)	*A* (2, 3)
3530·02 (0)	28320·4		
3512·9 (1)	28458	(1, 2)	*A* (1, 2)
3484·50 (8)	28690·3	(0, 1)	*A* (0, 1)
3475·87 (0)	28761·6	(3, 3)	*A* (3, 3)
3469·16 (0)	28817·2		
3444·64 (3)	29022·3	(2, 2)	*A* (2, 2)
3415·84 (5)	29267·0	(1, 1)	*A* (1, 1)
3406·94 (1)	29343·5	(4, 3)	
3388·26 (6)	29505·2	(0, 0)	*A* (0, 0)
3381·72 (2)	29562·3	(3, 2)	*A* (3, 2)
3374·66 (1)	29624·1	(6, 4)	
3351·4 (2)	29830	(2, 1)	*A* (2, 1)
3344·71 (1)	29889·4	(5, 3)	
3323·45 (7)	30080·6	(1, 0)	*A* (1, 0)
3316·80 (1)	30140·9	(7, 4)	
3316·22 (1)	30146·1	(4, 2)	
3291·80 (2)	30369·8	(3, 1)	*A* (3, 1)
3286·26 (1)	30421·0	(6, 3)	
3262·37 (6)	30643·8	(2, 0), (8, 4)	*A* (2, 0)
3257·64 (1)	30688·2	(5, 2)	
3229·76 (2)	30953·1	(4, 1)	
3205·79 (4)	31184·6	(3, 0)	*A* (3, 0)
3202·04 (2)	31221·1	(6, 2)	
3174·44 (1)	31492·5	(5, 1)	
3149·16 (1)	31738·3	(7, 2)	
3146·74 (2)	31769·6	(4, 0)	
3121·55 (1)	32026·1	(6, 1)	
3094·41 (0)	32307·0	(5, 0)	
3071·86 (0)	32544·1	(7, 1)	

progressions when v'' is constant can readily be seen; in fact the intensities of these progressions are comparable with those of the v'' progressions when v' is constant.

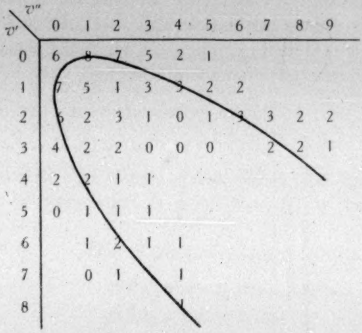
The addition of these bands, together with the estimated photographic intensities, enables the form of the Condon parabola to be examined. It will be seen

Table 2

v' v''	0		1		2		3		4		5		6		7		8		9
0	29505·2	814·9	28690·3	807·3	27883·0	800·6	27082·4	792·7	26289·7	783·5	25506·2								
	575·4		*576·7*		*575*		*574·2*		*575·5*		*574·0*								
1	30080·6	813·6	29267·0	808·4	(28458)	802	27656·6	791·4	26865·2	785·0	26080·2	783·1	25303·1						
	563·2		*563*		*564*		*564·9*		*565*		*562·6*		*563·7*						
2	30643·8	814	(29830)	808	29022·3	800·8	28221·5	791	(27430)	787	26642·8	776·0	25866·8	772·9	25093·9	763·2	24330·7	754·3	23576·4
	540·8		*540*		*540·0*		*540·1*		*537·7*		*540·5*				*544·4*		*541·9*		*545·7*
3	31184·6	814·8	30369·8	807·5	29562·3	800·7	28761·6	793·7	27967·7	784·4	27183·3				25638·3	765·7	24872·6	750·5	24122·1
	585·0		*583·3*		*583·8*		*581·9*												
4	31769·6	816·5	30953·1	807·0	30146·1	802·6	29343·5												
	537·4		*539·4*		*542·1*		*545·9*												
5	32307·0	814·5	31492·5	806·3	30688·2	798·8	29889·4												
			533·6		*532·9*		*531·6*												
6			32026·1	805·0	31221·1	800·1	30421·0		29624·1										
			518·0		*517·2*				*516·8*										
7			32544·1	805·8	31738·3				30140·9										
									502·9										
8									30643·8										

Brackets ( ) denote that the measurement is only approximate owing to overlapping bands.

from figure 2 that the parabola is of the wide type similar to those shown by the fourth positive bands of CO and the ultra-violet bands of SiO, which are oxides of the elements of the same group of the periodic table as tin.



v' \ v''	0	1	2	3	4	5	6	7	8	9
0	6	8	7	5	2	1				
1	7	5	1	3	3	2	2			
2	6	2	3	1	0	1	3	3	2	2
3	4	2	2	0	0	0		2	2	1
4	2	2	1	1						
5	0	1	1	1						
6		1	2	1	1					
7		0	1		1					
8					1					

Figure 2. Intensities of bands.

The equation for the origins of the bands of a system is

$$\nu = \nu_e + [\omega_e' (v' + \tfrac{1}{2}) - x_e'\omega_e' (v' + \tfrac{1}{2})^2 + y_e'\omega_e' (v' + \tfrac{1}{2})^3 \ldots]$$
$$- [\omega_e'' (v'' + \tfrac{1}{2}) - x_e''\omega_e'' (v'' + \tfrac{1}{2})^2 + y_e''\omega_e'' (v'' + \tfrac{1}{2})^3 \ldots],$$

where ω_e is the frequency of vibrations of the nuclei of infinitesimal amplitude;

$x_e, y_e, \ldots$ are small constants taking into account the fact that the vibrations are not quite harmonic;

v is the vibrational quantum number, taking successive integral values 0, 1, 2, 3, ...; and

the superscripts ′ and ″ refer to the upper and lower electronic states in accordance with the usual convention. ′, ″

The resolving power available was not sufficient to obtain data for the band origins, but a similar equation applies to the heads, if slightly different coefficients are used. There is also a term in $(v' + \tfrac{1}{2})(v'' + \tfrac{1}{2})$. This is usually small and it could not be determined for these bands. For the SnO band system under consideration the equation derived for the *R* heads is

$$\nu = 29626{\cdot}1 + [578{\cdot}9 (v' + \tfrac{1}{2}) - 1{\cdot}1 (v' + \tfrac{1}{2})^2 - 0{\cdot}32 (v' + \tfrac{1}{2})^3]$$
$$- [821{\cdot}9 (v'' + \tfrac{1}{2}) - 3{\cdot}6 (v'' + \tfrac{1}{2})^2].$$

It will be seen that a term in $(v' + \tfrac{1}{2})^3$ is required to express the vibrational levels of the upper state, whilst the coefficient y_e'' of $(v'' + \tfrac{1}{2})^3$ in the lower state is too small to be determined from the data obtained. There also appears to be a perturbation of the level $v'' = 3$, and this discontinuity is not taken into account by the above formula.

There is no indication that other branches form heads. This fact, together with the further fact that the ground states of several of the other oxides of this group of the periodic table (for instance CO*, SiO† and PbO‡) are all $^1\Sigma$ states, suggests that the ground state of the SnO molecule is also a $^1\Sigma$ state. The reason for considering that the lower state of this *A* system is the ground state will be seen from the absorption spectrum.

The perturbation of the vibrational level ($v' = 3$) indicated by the Δv values in table 2 is more clearly exhibited in figure 3, in which the wave-number differences between the bands in successive horizontal rows have been plotted.

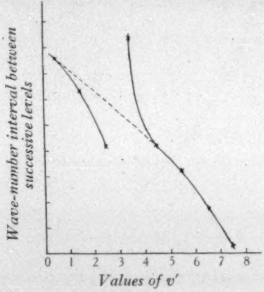


Figure 3.

It will be seen that the intervals between the bands associated with the levels 2 and 3 are smaller than would be expected, whilst the interval between the levels 3 and 4 is much larger than succeeding intervals. After the disturbance has been passed the intervals return to the regular curve, shown dotted near the perturbed level. W. Jevons§ has suggested that some of the so-called vibrational perturbations are actually due to a perturbation of one of the rotational levels, after which the later lines forming the band do not return to their regular positions. If the line structure is not resolved, measurement of the head would make it appear that the whole band was displaced. This may well be the cause of the apparent displacement of the level in the present case, but until the fine structure has been examined the question cannot be decided.

§8. ENERGY OF DISSOCIATION

Although it is not possible to follow the v'' progressions as far as the convergence point, an approximate value of the energy required to dissociate the nuclei when in the lower electronic state can be obtained by the extrapolation method of R. T. Birge and H. Sponer‖. This method assumes that the relation between $\Delta G(v)$

---

* C. P. Snow and E. K. Rideal, *Proc. R.S.* A, **125**, 462 (1929).

† P. G. Saper, *Phys. Rev.* **40**, 465 (1932).

‡ A. Christy and S. Bloomenthal, *Phys. Rev.* **35**, 46 (1930).

§ *Report on Band Spectra of Diatomic Molecules*, p. 203 (Phys. Soc. 1933).

‖ *Phys. Rev.* **28**, 259 (1926).

and v is linear. Within the degree of accuracy obtainable from the experimental data such an assumption is justifiable in this particular case. Examination of the equation giving the positions of the band heads shows that the interval between successive vibrational levels gradually decreases with increasing values of v until, at a certain value of v called $v_{\text{max.}}$, the interval vanishes.

$$v_{\text{max.}} = \omega_e/2x_e\omega_e - \tfrac{1}{2}.$$

This corresponds to the dissociation of the particular state, and by substituting the value of $v_{\text{max.}}$ in the vibrational energy term

$$G(v) = \omega_e(v + \tfrac{1}{2}) - x_e\omega_e(v + \tfrac{1}{2})^2$$ **G**

we obtain the value of D_e, the energy of dissociation from the equilibrium position. **D_e** The actual energy of dissociation D is less than D_e by the energy of the lowest **D** vibrational level, $v = 0$.

Hence
$$\begin{aligned} D &= G(v_{\text{max.}}) - G(0) \\ &= \omega_e^2/4x_e\omega_e - \tfrac{1}{2}\omega_e + \tfrac{1}{4}x_e\omega_e \\ &= \tfrac{1}{2}v_{\text{max.}}(\omega_e - x_e\omega_e). \end{aligned}$$

The value of the energy of dissociation D'' in the lower electronic state is thus **D''** given by

$$\begin{aligned} D'' &= \tfrac{1}{2} \times 113\cdot6 \times 818\cdot3 \text{ cm}^{-1} \\ &= 5\cdot7 \text{ volts.} \end{aligned}$$

Owing to the apparent perturbation of the level $v' = 3$, the vibrational constants of the upper state cannot be determined with sufficient accuracy to determine the energy of dissociation D' of this state by extrapolation.

§ 9. MAHANTI'S *B* AND *C* SYSTEMS

The formulae given by Mahanti for the band heads in his three systems are as follows:

For the *A* system

$$\begin{aligned} \nu = 29630\cdot5 &+ [586\cdot0(v' + \tfrac{1}{2}) - 6\cdot0(v' + \tfrac{1}{2})^2] \\ &- [824\cdot0(v'' + \tfrac{1}{2}) - 4\cdot0(v'' + \tfrac{1}{2})^2]. \end{aligned}$$

For the *B* system

$$\begin{aligned} \nu = 25418\cdot6 &+ [637\cdot0(v' + \tfrac{1}{2}) - 8\cdot0(v' + \tfrac{1}{2})^2] \\ &- [824\cdot0(v'' + \tfrac{1}{2}) - 4\cdot0(v'' + \tfrac{1}{2})^2]. \end{aligned}$$

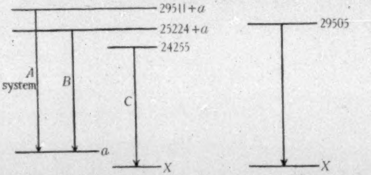
For the *C* system

$$\begin{aligned} \nu = 24370\cdot4 &+ [582\cdot0(v' + \tfrac{1}{2}) - 4\cdot0(v' + \tfrac{1}{2})^2] \\ &- [813\cdot5(v'' + \tfrac{1}{2}) - 5\cdot5(v'' + \tfrac{1}{2})^2]. \end{aligned}$$

Since the values of ω_e and $x_e\omega_e$ shown above are the same for the lower levels of the *A* and the *B* systems, these transitions should evidently have the same final electronic state. The constants of both the levels of the *C* system are slightly different from those associated with any of the electronic levels so far considered.

The transitions according to Mahanti are those shown on the left of figure 4. For comparison, the author's suggested scheme is shown on the right.

There was no spectroscopic evidence to show which of the levels a or X was the lower, but by comparing the value of the energy of dissociation, deduced from extrapolation of the vibrational levels of the lower electronic state of the C system, with the thermochemical value, Mahanti decided that the level X was the ground state. Such extrapolations are, however, only approximate, even when accurate data are available, so that in the present instance, where there are only a small number of bands in the system, the value of the energy of dissociation may be considerably in error.



Mahanti's classification *Levels found by author*

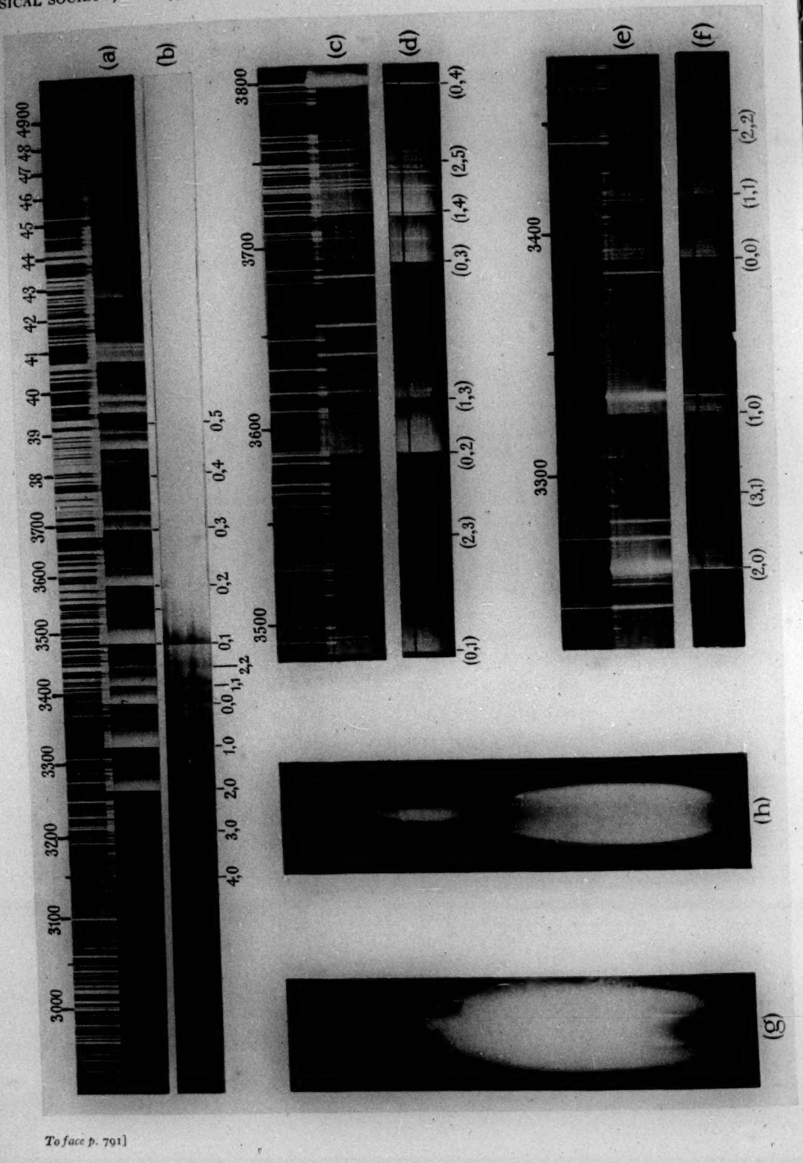
Figure 4.

Examination of the absorption spectrum, shown at (*b*) in the plate, showed that only bands of the A system appeared. Owing to the relatively high temperature at which absorption was occurring, not only was the v' progression (0, 0), (1, 0), (2, 0), ... visible, but also the (0, 1), (1, 1), (2, 1), ..., which appeared with much lower intensity. This is, of course, to be expected, since there is probably an appreciable concentration of SnO molecules in the states $v'' = 1$ or even 2, at the temperature of the hydrogen flame. The temperature could be reduced by mixing nitrogen with the hydrogen supplied to the burner. But the reduced intensity of the flame prevented any great use of this method from being made.

There was no sign of the B system in the absorption spectrum, although this, according to Mahanti, has the same final level and is actually a more probable transition, since less energy would be required than for the production of the A system.

The presence of the A system alone in absorption suggests that the lower electronic state in this system must be the ground state of the molecule. In spite of the similarity in some of the vibrational constants, the final level of the so-called B system cannot also be the ground state. The actual existence of the principal bands in the B and C systems has been confirmed, but it is very doubtful, in view of the small number of bands in each system, their weak intensities, and the evidence given by absorption, whether these bands really do form parts of separate systems. At the same time it must be admitted that it has not been found possible to incorporate the bands concerned into the principal A system.

The possibility of the upper electronic level being triple has also been con-


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
4900
48
47
46
45
44
43
42
41
40
39
38
3700
3600
3500
3400
3300
3200
3100
3000
0,5
0,4
0,3
0,2
0,1
2,2
1,1
0,0
1,0
2,0
3,0
4,0
3800
3700
3600
3500
(0,4)
(2,5)
(1,4)
(0,3)
(1,3)
(0,2)
(2,3)
(0,1)
3400
3300
(2,2)
(1,1)
(0,0)
(1,0)
(3,1)
(2,0)

sidered, but no satisfactory arrangement has been found. It is also possible that the spectrum is due to a polyatomic oxide molecule. In addition to these bands of Mahanti's B and C systems, there are a number of other bands which remain unclassified. These were not recorded by Mahanti.

§ 10. ACKNOWLEDGMENT

The author wishes to express sincere thanks to Prof. A. Fowler, F.R.S., for valuable advice during the work, and to Dr W. Jevons and Dr R. W. B. Pearse for many helpful suggestions.

DESCRIPTION OF PLATE

(*a*) General view of spectrum of SnO in flame source, with the Hilger E 2 quartz spectrograph. To avoid confusion only the principal bands are marked.

(*b*) Absorption spectrum on same scale as (*a*), showing v' progressions ($v'' = 0$ and 1).

(*c*) and (*e*) Parts of spectrum of metallic arc in air under higher dispersion, with the Hilger E 1 quartz Littrow.

(*d*) and (*f*) Spectrum obtained from high-tension arc in flame. Bands are intermediate in character between flame (*a*) and arc (*c*) and (*e*). Note comparative freedom from interference by extraneous spectra.

(*g*) Flame of hydrogen containing stannic-chloride vapour. The inner region is yellow, the outer mantle bright blue.

(*h*) Similar flame to (*g*), but with nitrogen mixed with hydrogen. The yellow region is now above rest of flame.

550.83 : 519.281.2

THE RAPID ADJUSTMENT OF OBSERVATIONS IN A NETWORK OF GEOPHYSICAL STATIONS BY THE METHOD OF LEAST SQUARES

By E. LANCASTER JONES, B.A.

Communicated by Prof. A. O. Rankine, July 28, 1933

ABSTRACT. A frequent problem in geodesy and geophysics concerns the adjustment of a set of values for a physical magnitude at a number of stations. The values are obtained from other observed magnitudes by computations involving the geometrical links of the station network, and there is ambiguity on account of the multiplicity of connections. Since the magnitude desired is single-valued at each station, the values obtained are usually adjusted by the method of least squares. Where the number of stations is large and the network is complex, the normal equations for least-square adjustment are very numerous and their solution by standard procedure is tedious. The paper develops a method of establishing the normal equations, and solving them by successive approximations, which is simple, rapid and satisfactory in practice, and is applicable to any network, however large and complex. Although particular attention is focused on the problem of obtaining isogams from observations of gravity gradients in applied geophysics, the method has obvious applications in other fields where the mathematical conditions are similar.

---

§ 1. INTRODUCTION

In many branches of geodesy and geophysics, observations of physical magnitudes are made at a series of stations which form a network of triangles or polygons. From these measured magnitudes it is frequently desired to compute the values of other magnitudes at the stations concerned. By reason of the relationship between the observed and computed magnitudes, and the geometry of the network, it usually happens that there is ambiguity in the final values attained, and it is customary to apply the method of least squares to resolve the ambiguity.

g_B, g_A

y_1, x_2, y_2
$X_1, Y_1,$
X_2, Y_2

A particular example occurs in applied geophysics in the computation of isogams from observations of the gradients of gravity at stations of the network. The difference in gravity $g_B - g_A$ at two stations A, B of the network may be obtained by taking any path formed of straight lines joining adjacent stations between A and B, assuming that the average gradient of gravity along the rectilinear sections of the path is equal to the mean of the values at the two stations connected by it, and taking the sum of the sectional differences of gravity thus computed. Thus, if P and Q are any two consecutive stations on the path chosen, and if their co-ordinates are (x_1, y_1) and (x_2, y_2) whilst their component gravity-gradients are (X_1, Y_1) and (X_2, Y_2) respectively, we have

$$2(g_B - g_A) = \Sigma_A^B [(X_1 + X_2)(x_2 - x_1) + (Y_1 + Y_2)(y_2 - y_1)].$$

If, however, we take another path connecting A to B and involving other intervening stations, we shall usually obtain a different value for $g_B - g_A$.

This is a particular case of a more general problem concerned with single-valued functions, and it is with this general class that we are concerned.

§ 2. THE PROBLEM

Given a network of stations $A, B, C, \ldots$ and the observed or computed values of the increments (ab), (bc), (ca), ... between adjacent stations of a single-valued function U, we have to find the best possible values of U at $A, B, C, \ldots$.

The problem resolves itself into one which may be expressed thus: To find the adjusted values (AB), (BC), (CA), ... of the increments (ab), (bc), (ca), ..., respectively, where, around any closed polygonal path $ABC \ldots PA$, we have the condition that

$$(AB) + (BC) + (CD) + \ldots + (PA) = 0,$$

whereas, in general

$$(ab) + (bc) + (cd) + \ldots + (pa) \neq 0 \text{ but} = \text{some value } d.$$

We may call d the "excess" around the path $ABC \ldots PA$.

In the particular cases of gravitational and magnetic observations in applied geophysics, this problem and its solution by the method of least squares have been considered by I. Roman*. Roman states the problem in a different but equivalent manner and obtains rather more complex normal equations, which he solves by the usual reduction method of Gauss.

The present writer believes that the treatment given below is particularly adapted to this problem. The normal equations are simple and can be written down by inspection. Methods of resolution of these equations are suggested which are much less laborious than the Gaussian reduction methods, and permit the labour of reduction to be accommodated to the particular degree of accuracy in adjustment which is considered worth while. Most practical geophysicists are agreed that an elaborate, ultra-precise least-square adjustment of their observations is an unwarranted expenditure of time and labour. On the other hand, some adjustment is obviously necessary.

§ 3. THE NORMAL EQUATIONS

In the terms used in treatises on the method of least squares†, we have given a series of "conditional" equations

$$\begin{aligned} (AB) &= (ab), \\ (BC) &= (bc), \\ (CA) &= (ca), \\ &\ldots\ldots\ldots\ldots\ldots \end{aligned}$$

---

* *Trans. Amer. Inst. Min. Metall. Engrs.* "Geophysical Prospecting", 460 (1932).

† Whittaker, E. T. and Robinson, G., *The Calculus of Observations*, chap. IX, and particularly § 129, pp. 252–254 (1924).

together with a series of "rigorous" equations

$$(AB) + (BC) + (CA) = 0,$$

$$\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots$$

There is one conditional equation for every link in the network, and one rigorous equation for every *independent* polygon in the network. We shall assume that all the observations and link-increments such as (ab) have equal weight.

For such a system of conditional and rigorous equations, the normal equations for a least-square adjustment are obtained as follows. For each rigorous equation, provide an unknown multiplier or correlate m. The unknown increment (PQ), which occurs in one only of the conditional equations, namely $(PQ) - (pq) = 0$, occurs also in at most two of the rigorous equations. For normally it will be a common section of the boundary of two adjacent polygons, e.g. $OPQR$, $SQPT$, figure 1, and at the extreme boundaries of the network one of these polygons will be absent. The increments (pq), (PQ) are of course algebraical quantities, so that $(pq) = -(qp)$, $(PQ) = -(QP)$.

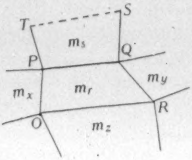


Figure 1.

If we assume that the polygonal circuits such as $OPQR$ are always traversed in the same direction, e.g. clockwise, then (PQ) occurs positively in $OPQR$, but negatively in $SQPT$.

For such a link as (PQ) there will result a normal equation

$$(PQ) = (pq) - m_r + m_s \qquad \dots\dots(1),$$

m_r, m_s where m_r and m_s are the multiplier correlates attached to the polygons $OPQR$ and $SQPT$ respectively.

Similarly for every other link, except on the boundary of the network where one of the m's will be absent.

Since the rigorous equations continue to be satisfied, we can replace every term such as (PQ) in them by its equivalent in the above equation. We thus get a series of equations, one for each independent polygon, of the form (see figure 1).

$$(op) - m_r + m_x + (pq) - m_r + m_s + (qr) - m_r + m_y + (ro) - m_r + m_z = 0,$$

where the polygons x, y and z as well as s also touch polygon r at OP, QR and RO respectively.

Thus, for a four-sided polygon r, having contacts with four others x, s, y and z, we have an equation

$$4m_r - m_x - m_s - m_y - m_z = (op) + (pq) + (qr) + (ro)$$
$$= d_r,$$

where d_r is the observed or computed excess around the polygon. Similarly, for an n_r-sided polygon r, which has contacts with adjacent polygons x, s, y, ... , we have an equation d_r n_r

$$n_r m_r - m_x - m_s - m_y - ... = d_r \qquad ......(2).$$

There is one such equation for each independent polygon of the network, so that, for the set of unknown multipliers or correlates m, we have an equal number of linear equations such as (2). From these we can obtain uniquely each of the correlates $m_1, m_2, ...$, and by using equations (1) we can then obtain quite simply each adjusted link increment (PQ). The whole procedure thus hinges on the solution of the set of correlate equations (2). As has been stated and demonstrated above, these can be written down for any network by inspection.

§4. SOLUTION OF THE CORRELATE EQUATIONS. APPROXIMATIONS

The series of correlate equations of the type

$$n_r m_r - \Sigma m_x = d_r$$

can be solved by any of the methods appropriate to linear equations, including that of Gauss. This series is, however, obviously adapted to solution by gradual approximation. Every coefficient is unity except those for the key correlates such as m_r, and these are integers not less than 3.

As a first approximation, we can put

$$m_r = m_r' + \Delta m_r,$$

where $$m_r' = d_r/n_r.$$ m_r'

Similarly $$m_x' = d_x/n_x \qquad ......(3),$$
$$m_y' = d_y/n_y,$$
$$..............$$

whence $$\Delta m_r = \frac{1}{n_r}\Sigma m_x = \frac{1}{n_r}\Sigma d_x/n_x + \frac{1}{n_r}\Sigma\Delta m_x.$$

Writing $$m_r'' = \frac{1}{n_r}\Sigma d_x/n_x \qquad ......(4),$$ m_r''

we have $m_r' + m_r''$ as a second approximation to m_r.

Similarly we can find the values m_x'', m_s'', ... and obtain a third approximation $m_r' + m_r'' + m_r'''$ to m_r by writing

$$m_r''' = \frac{1}{n_r}\Sigma m_x'' \qquad ......(5).$$ m_r'''

The procedure can be continued as far as desired, and can be terminated at any stage when the added increments to m_r', m_r'', m_r''', ... become sufficiently small. It is simple and lends itself to routine execution.

Although exact solutions for particular networks, and methods of more rapid approximation, will be discussed later, we may test this particular method for the case discussed by Roman in the paper previously cited.

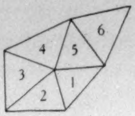


Figure 2.

Figure 2 illustrates the network solved by Roman. There are seven station points and six triangles. In table 1, column d gives the original excesses for each triangle. The successive approximations to the m's are calculated from these d's and the previously obtained approximations for the adjacent triangles given in the third column.

Table 1

Δ	d	Adjacent Δs	m'	$3m''$	m''	$3m'''$	m'''	$3m^{\text{iv}}$	m^{iv} …
1	+ 5	2 + 5	1·667	5	1·667	− 3·333	− 1·111	0·741	0·247 …
2	+ 10	1 + 3	3·333	− 1·666	− 0·556	0·556	0·185	− 1·481	− 0·494 …
3	− 10	2 + 4	− 3·333	− 3·334	− 1·111	− 0·110	− 0·370	− 1·111	− 0·370 …
4	− 20	3 + 5	− 6·667	− 1·666	− 0·556	− 3·889	− 1·296	0·186	0·062 …
5	+ 5	1 + 4 + 6	1·667	− 8·333	− 2·778	1·667	0·556	− 3·333	− 1·111 …
6	− 10	5	− 3·333	1·667	0·556	− 2·778	− 0·926	0·556	0·185 …

The residuals do not disappear very rapidly, but the procedure is easy and rapid.

The values for m obtained by summing the first four elements m' to m^{iv} are within 1·0 of the correct values, and would be quite near enough in practice for obtaining the values of gravity at the stations and drawing up the isogam chart. The original link-increments from which the d's were calculated were of the order of 50 units, so that the final values adjusted on the basis of this fourth approximation would be correct within 2 per cent, which is the limit for gravity work of this type. The final values, obtained by putting m equal to $m' + m'' + m''' + m^{\text{iv}}$ are $m_1 = 2·47$, $m_2 = 2·47$, $m_3 = -5·19$, $m_4 = -8·46$, $m_5 = -1·67$, $m_6 = -3·52$, which should be compared with the values obtained in the next section.

A more rapid approximation in the solution of the set of correlate equations

$$n_r m_r - \Sigma m_x = d_r$$

can be obtained by solving partially for those which involve m_r, as follows.

We have, say,

$$\begin{aligned}
n_r m_r - m_x - m_s - m_y - m_z &= d_r,\\
n_x m_x - m_r - m_a - m_b - \dots &= d_x,\\
n_s m_s - m_r - m_e - m_f - \dots &= d_s,\\
n_y m_y - m_r - m_h - m_k - \dots &= d_y,\\
n_z m_z - m_r - m_p - m_q - \dots &= d_z.
\end{aligned}$$

From which we can obtain, by dividing the second by n_x, third by n_s, ... and adding

$$m_r\left(n_r - \Sigma\frac{1}{n_x}\right) - \Sigma\frac{1}{n_x}(m_a + m_b + \ldots) = d_r + \Sigma\frac{d_x}{n_x}.$$

For a first approximation m_r' we can put

$$m_r' = \left(d_r + \Sigma\frac{d_x}{n_x}\right)\Big/\left(n_r - \Sigma\frac{1}{n_x}\right) \qquad \ldots\ldots(6),$$

and subsequent increments to this are given by

$$m_r'' = \left(\Sigma\frac{1}{n_x}(m_a' + m_b' + \ldots)\right)\Big/\left(n_r - \Sigma\frac{1}{n_x}\right) \qquad \ldots\ldots(7),$$

$$m_r''' = \left(\Sigma\frac{1}{n_x}(m_a'' + m_b'' + \ldots)\right)\Big/\left(n_r - \Sigma\frac{1}{n_x}\right) \qquad \ldots\ldots(8),$$

……………………………………

When all the polygons concerned have the same number n of sides, the formulae become n

$$m_r' = (nd_r + \Sigma d_x)/(n^2 - n_r') \qquad \ldots\ldots(9),$$

where n_r' is the number of polygons adjacent to, or at "first remove" from, the key polygon r. n_r'

Also

$$\left.\begin{aligned} m_r'' &= \Sigma m_a'/(n^2 - n_r') \\ m_r''' &= \Sigma m_a''/(n^2 - n_r') \\ &\ldots\ldots\ldots\ldots\ldots\ldots \end{aligned}\right\} \qquad \ldots\ldots(10),$$

Here Σ denotes the series of polygons excluding r which are at second remove from r, i.e. are adjacent to these at first remove from r.

We can again illustrate this system of approximation with reference to the network of six triangles previously considered, figure 2. Table 2 defines the constants concerned in each triangle, n being equal to 3 throughout.

Table 2

Δ	d	1st-remove Δs	2nd-remove Δs	$n^2 - n_r'$	$nd_r + \Sigma d_x$
1	+ 5	2, 5	3, 4, 6	7	30
2	+ 10	1, 3	4, 5	7	25
3	− 10	2, 4	1, 5	7	− 40
4	− 20	3, 5	1, 2, 6	7	− 65
5	+ 5	1, 4, 6	2, 3	6	− 10
6	− 10	5	1, 4	8	− 25

In table 3, where $N_r = n^2 - n_r'$, the approximations are shown worked out to m^{v}, at which stage the residues are well below 0·1 and the values obtained for the m's are within 0·02 of the correct values. This would be an over-elaborate refinement in practice, but illustrates the rapidity of approximation obtainable by the method. N_r

Table 3

N	Δ	m'	Δ''	$+\ m''\ -$	$+\ m'''\ -$	$+\ m^{\text{iv}}\ -$	$+\ m^{\text{v}}\ -$	m
7	1		3	5·714	0·374	0·421	0·020	4·347
			4	9·286	0·676	0·683	0·019	− 2·798
			6	3·125	0·625	0·239	0·078	
				18·125	0·425	1·343	0·117	
		4·286	m	− 2·589	0·061	− 0·192	− 0·017	1·549
7	2		4	9·286	0·676	0·683	0·019	3·617
			5	1·667	0·357	0·199	0·063	− 1·703
				10·953	0·319	0·882	0·082	
		3·571	m	− 1·565	0·046	− 0·126	− 0·012	1·914
7	3		1	4·286	2·589	0·061	0·192	0·374
			5	1·667	0·357	0·199	0·063	− 6·191
				2·619	2·946	0·138	0·255	
		− 5·714	m	0·374	−0·421	− 0·020	− 0·036	− 5·817
7	4		1	4·286	2·589	0·061	0·192	
			2	3·571	1·565	0·046	0·126	0·676
			6	3·125	0·625	0·239	0·078	− 10·045
				4·732	4·779	0·132	0·396	
		− 9·286	m	0·676	− 0·683	− 0·019	− 0·059	− 9·369
6	5		2	3·571	1·565	0·046	0·126	
			3	5·714	0·374	0·421	0·020	
				2·143	1·191	0·375	0·146	
		− 1·667	m	− 0·357	− 0·199	− 0·063	− 0·024	− 2·310
8	6		1	4·286	2·589	0·061	0·192	
			4	9·286	0·676	0·683	0·019	
				5·000	1·913	0·622	0·211	
		− 3·125	m	− 0·625	− 0·239	− 0·078	− 0·026	− 4·093

The final values obtained are

$$m_1 = 1{\cdot}55,\quad m_2 = 1{\cdot}91,\quad m_3 = -\,5{\cdot}82,\quad m_4 = -\,9{\cdot}37,\quad m_5 = -\,2{\cdot}31,\quad m_6 = -\,4{\cdot}09.$$

§ 5. RECTANGULAR NETWORKS

The case of a rectangular network has a particular importance, since it corresponds to an ideal arrangement of stations often used in practical geophysical surveys on suitable terrain.

Referring to equations (9) and (10) of § 4, we have

$$n = 4 \quad\text{and}\quad n_r' = 1,\ 2,\ 3 \text{ or } 4 \text{ generally.}$$

$$\therefore\quad N_r = n^2 - n_r' = 12,\ 13,\ 14 \text{ or } 15,$$

and we can solve by successive approximation, as in the case of triangles, using the formulae

$$\left.\begin{aligned} m_r' &= (4d_r + \Sigma d_x)/N_r \\ m_r'' &= \Sigma m_a'/N_r \\ m_r''' &= \Sigma m_a''/N_r \\ &\ldots\ldots\ldots\ldots\ldots\ldots \end{aligned}\right\} \qquad \ldots\ldots(11),$$

which give approximations approaching the complete solution m_r with rapidity rather greater than in the case of triangles.

It should be carefully noted that, throughout the above reasoning, we have assumed that each first-remove and second-remove polygon is independent. If any polygon occurs as a common second-remove to two first-remove polygons, it must be counted twice in the sums $\Sigma m_a'$, $\Sigma m_a''$, ...

§ 6. SOLUTIONS OF INCREASING PRECISION. RECTANGULAR NETWORKS

In networks which have a regular pattern, whether of triangles or rectangles, formulae can be developed for expressing the correlate of any particular figure (polygon) in terms of the excesses of its surrounding figures, to any degree of remoteness.

Previously we have only considered the elimination of the first-remove polygons, leaving the second-remove ones as first residuals. We next consider how to eliminate polygons of second and greater remoteness.

Figure 3 shows a rectangular network in which the rectangles are numbered from one corner 00 in rows and columns.

00	01	02	03	04
10	11	12	13	14
20	21	22	23	24
30	31	32	33	34

Figure 3.

Any rectangle has a number of first-remove rectangles varying from 2 to 4 according to its position at a corner of the complete network, on the outer run or in the interior of the network.

From the geometry, each first-remove rectangle may have contact with a second-remove rectangle which is common to another first remove. For instance, 11 is common to 01 and 10, both first removes of 00.

We shall first find expressions for the correlate of any rectangle, eliminating both the first-remove and the common second-remove correlates. The corner rectangle 00 has two first removes and one common second remove, and the correlate equations are

$$\begin{aligned} 4m_{00} - m_{01} - m_{10} \qquad\qquad\qquad\qquad &= d_{00}, \\ -\ m_{00} + 4m_{01} \qquad - m_{11} - m_{02} \qquad &= d_{01}, \\ -\ m_{00} \qquad + 4m_{10} - m_{11} \qquad - m_{20} &= d_{10}, \\ -\ m_{01} - m_{10} + 4m_{11} - m_{12} - m_{21} &= d_{11}. \end{aligned}$$

m_{rs}, d_{rs}

Multiplying the equations by 7, 2, 2 and 1 respectively and adding, we eliminate m_{01}, m_{10} and m_{11} and obtain

$$24m_{00} - 2\,(m_{02} + m_{20}) - (m_{12} + m_{21}) = 7d_{00} + 2\,(d_{01} + d_{10}) + d_{11} \qquad \ldots\ldots(12),$$
$$= 24D_{00},\text{ say,}$$

D_{rs}

and $m_{00}' = D_{00}$ gives a good approximation to m_{00}, which can be continued by writing

m_{rs}', m_{rs}'', m_{rs}'''

$$m_{00} = m_{00}' + m_{00}'' + m_{00}''' + \ldots,$$

where
$$24m_{00}'' = 2\,(m_{02}' + m_{20}') + m_{12}' + m_{21}',$$
$$24m_{00}''' = 2\,(m_{02}'' + m_{20}'') + m_{12}'' + m_{21}'',$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

and these m_{02}', m_{20}', ... are approximations similarly obtained. The rectangles such as 01, 02, ... , 10, 20, ... , which are on the boundary but not in corners, have each three first-remove and two common second-remove rectangles. Two of the first removes are on the boundary and one is in the interior; this third interior rectangle touches both the common second removes.

For 01, for instance, the correlate equations are expressed as shown in table 4, by means of the coefficients only, all applicable to any one m being in the same column while all applicable to any one rectangle are in the same row as its excess d.

Table 4

d	m_{01}	m_{00}	m_{11}	m_{02}	m_{10}	m_{12}	Residues
01	4	− 1	− 1	− 1			
00	− 1	4			− 1		
11	− 1		4		− 1	− 1	$-m_{21}$
02	− 1			4		− 1	$-m_{03}$
10		− 1	− 1		4		$-m_{20}$
12			− 1	− 1		4	$-m_{13}-m_{22}$

Multiplying by 52, 15, 17, 15, 8 and 8 respectively and adding, we get

$$161m_{01} - 17m_{21} - 15m_{03} - 8\,(m_{20} + m_{13} + m_{22}) = 161D_{01} \qquad \ldots\ldots(13),$$

where
$$161D_{01} = 52d_{01} + 17d_{11} + 15\,(d_{00} + d_{02}) + 8\,(d_{10} + d_{12})$$

and $m_{01}' = D_{01}$ gives a first approximation to m_{01}. It should be noted that all the rectangles whose correlates are thus eliminated are those which are laterally and diagonally once-removed from the key rectangle 01, whilst the residual correlates m_{20}, m_{21}, m_{22}, m_{03} and m_{13} are the ones adjacent externally to those eliminated.

Similarly for 02 we should get

$$161m_{02} - 17m_{22} - 15\,(m_{00} + m_{04}) - 8\,(m_{10} + m_{21} + m_{23} + m_{14})$$
$$= 52d_{02} + 17d_{12} + 15\,(d_{01} + d_{03}) + 8\,(d_{11} + d_{13}),$$

and so on for any other boundary rectangle not a corner.

The drawback to the above series for $m_{01}, m_{02}, \ldots$ is that the coefficients involved are not so simple as in the case of equations (11) and (12). There is some advantage in using for these rectangles the same multipliers, namely 7, 2 and 1 for the key equation, for all first-remove equations and for common second-remove equations, as were used in equation (12).

These give the equation

$$22m_{01} - m_{11} - 2\,(m_{21} + m_{03}) - (m_{20} + m_{13} + m_{22}) = 7d_{01} + 2\,(d_{00} + d_{11} + d_{02}) + d_{10} + d_{12}$$
$$= 22D_{01}' \qquad \ldots\ldots(14),$$

in which m_{11} is left as an additional residual to the previous series; but the series of residuals left for m_{01}'', after we have written

$$m_{01} = m_{01}' + m_{01}'' + \ldots \quad \text{and} \quad m_{01}' = D_{01}',$$

is very easy to use for further approximation.

For the inner rectangles, such as 11, 12, 21, 22, ..., which have four first-remove and four common second-remove rectangles, together forming a rectangle of three by three cells, we use multipliers 6, 2 and 1 respectively for each order of remoteness and obtain

$$20m_{11} - 2\,(m_{13} + m_{31}) - (m_{03} + m_{23} + m_{32} + m_{30})$$
$$= 6d_{11} + 2\,(d_{01} + d_{12} + d_{21} + d_{10}) + (d_{00} + d_{02} + d_{22} + d_{20}),$$
$$20m_{12} - 2\,(m_{10} + m_{32} + m_{14}) - (m_{00} + m_{04} + m_{24} + m_{33} + m_{31} + m_{20})$$
$$= 6d_{12} + 2\,(d_{11} + d_{02} + d_{13} + d_{22}) + (d_{01} + d_{03} + d_{23} + d_{21}),$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \qquad \ldots\ldots(15)$$

in which the residual m's multiplied by the coefficient 2 belong to all those rectangles in external contact with the first-remove rectangles, and those multiplied by the coefficient unity belong to those rectangles in contact with the common second-remove rectangles. There may be as many as four of the former and eight of the latter.

By a similar procedure of selecting suitable multipliers and summing the equations, it is possible to obtain for any correlate formulae which involve the elimination of all or most of the correlates of cells which are adjacent to the key cell, and therefore give a better first approximation than the preceding equations (11), (12), (14) and (15). This advantage is, however, more than counterbalanced by the increasing complexity of the residuals and series of excess terms, and for practical purposes either equations (11) or equations (12), (14) and (15) are recommended for use with a rectangular network.

Single chain of rectangles. In the particular case of a single chain of rectangles, as in figure 4

$S-4$	$S-3$	$S-2$	$S-1$	S	$S+1$	$S+2$	$S+3$	$S+4$

Figure 4.

there is some advantage in forming the equation for any correlate m of cell S, by eliminating pairs of cells on either side of it as far as symmetry permits, say, to the cells $S-3$ and $S+3$. We have the correlate equation coefficients shown in table 5.

Table 5

m									d	$\times$ *by*
$S-4$	$S-3$	$S-2$	$S-1$	S	$S+1$	$S+2$	$S+3$	$S+4$		
			-1	4	-1				$=S$	56
		-1	4	-1					$=S-1$	15
				-1	4	-1			$=S+1$	15
	-1	4	-1						$=S-2$	4
					-1	4	-1		$=S+2$	4
-1	4	-1							$=S-3$	1
						-1	4	-1	$=S+3$	1

And using the multipliers 1 for $S-3$ and $S+3$, 4 for $S-2$ and $S+2$, $(4\times 4-1)$ or 15 for $S-1$ and $S+1$, and $(4\times 15-4)$ or 56 for S, and adding, we get

$$194m_S - m_{S-4} - m_{S+4} = 56d_S + 15\,(d_{S-1}+d_{S+1}) \\ + 4\,(d_{S-2}+d_{S+2}) + (d_{S-3}+d_{S+3}) \quad \text{......(16)},$$

which gives a very rapid approximation for any central cell S. For cells near and at the ends of the chain the same multipliers are valid, but the residual m's have slightly different coefficients. For example, if the chain terminates in $S+2$, the above equation still holds for m_S if the term $-m_{S+4}$ on the left is replaced by $+m_{S+2}$ and d_{S+3} is omitted on the right.

The series of multipliers available for such a single chain of rectangular cells is the series

$$1,\ 4,\ 15,\ 56,\ \ldots\ p_r,$$

p_r where

$$p_r = 4p_{r-1} - p_{r-2} \quad \text{......(17)},$$

for any positive integral value of r,

and

$$p_1 = 1,\ p_2 = 4.$$

§ 7. TRIANGULAR NETWORKS. MORE RAPID APPROXIMATIONS

As in the case of the rectangular networks just considered, so in triangular networks can more rapid approximations for the correlate of any cell be obtained by eliminating the correlates for second- as well as first-remove triangles.

As the triangles will normally be restricted to those in which no angle is less than 45° and none greater than 90°, we can assume that only rare instances will occur of common second-remove cells. The normal case will be one in which each triangular cell has from one to three first-remove triangles touching it, and each of these has one or two independent second-remove triangles in external contact with it.

Single chain of triangles. Consider the case of figure 5, which relates to triangular cells in the same way that figure 4 relates to rectangular cells.

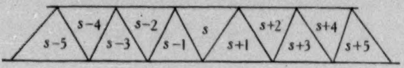


Figure 5.

The table of correlate equations with cell 5 as centre is shown in table 6.

Table 6

m											d
$S-5$	$S-4$	$S-3$	$S-2$	$S-1$	S	$S+1$	$S+2$	$S+3$	$S+4$	$S+5$	
				−1	3	−1					S
			−1	3	−1						$S-1$
					−1	3	−1				$S+1$
		−1	3	−1							$S-2$
						−1	3	−1			$S+2$
	−1	3	−1								$S-3$
							−1	3	−1		$S+3$
−1	3	−1									$S-4$
								−1	3	−1	$S+4$

As before, we can find a series of multipliers, namely

$$1, 3, 8, 21, 55, \dots p_{r-2}, p_{r-1}, p_r \dots,$$

where

$$p_r = 3p_{r-1} - p_{r-2} \qquad \text{......(18)},$$
$$p_2 = 3,$$
$$p_1 = 1,$$

which will eliminate all the correlates of intermediate pairs of triangles down to any desired residue, e.g. $S \pm 5$. For example, to eliminate from $S \pm 1$ to $S \pm 4$ inclusive, we use the series to the 5th term 55 and get

$$123m_S - m_{S-5} - m_{S+5} = 55d_S + 21\,(d_{S-1} + d_{S+1}) + 8\,(d_{S-2} + d_{S+2}) + 3\,(d_{S-3} + d_{S+3}) + d_{S-4} + d_{S+4} \qquad \text{......(19)}.$$

For cells near or at a terminus of the chain, we use the same series of multipliers.

For triangles with two second-remove cells to each first-remove cell we use the multiplier series 1, 3, 7; for instance, in the network of figure 6*a*, cell 0 has one first-remove cell 11 and this has two second-remove cells, 21 and 22.

The correlate table for m_0 is table 7.

Table 7

0	11	21	22	d	p
3	−1			0	7
−1	3	−1	−1	11	3
	−1	−3		21	1
	−1		3	22	1

whence, multiplying (see column p) by 7, 3, 1 and 1 respectively,

$$18m_0 = 7d_0 + 3d_{11} + d_{21} + d_{22} \qquad \text{......(20)}.$$

Similarly, in the network of figure 6*b*, we should get

$$12m_0 = 7d_0 + 3(d_{11} + d_{12} + d_{13}) + d_{21} + d_{22} + d_{23} + d_{24} + d_{25} + d_{26} \quad \text{......(21)}.$$

n_1 The coefficient of m_0 is always $21 - 3n_1$, where n_1 is the number of first-remove cells.

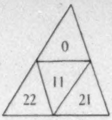


Figure 6 *a*.

If in the network of triangles actually under consideration there are third-remove triangles, or triangles of still greater remoteness from the key triangle for which approximation is desired, there will be residual correlates, $m_{31}, m_{32}, \ldots$, introduced into equations of type (19) and (20). There is no difficulty in finding series of multipliers to carry the elimination to further stages, especially if the cells are arranged symmetrically about the key cell. For example, the network of figure 6*b* may be completed by the insertion of three triangles 31, 32 and 33 between 22 and 23, and 24 and 25, and 26 and 21 respectively, giving three extra common third-remove triangles. The desired series of multipliers is then 2, 3, 7 and 15 and we get

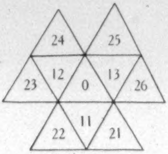


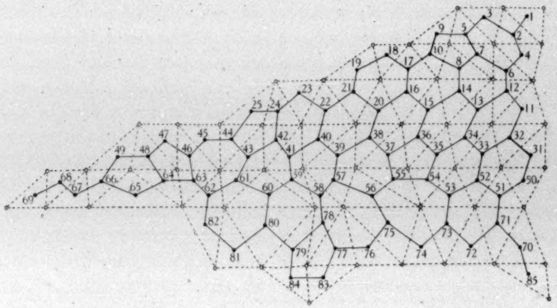
Figure 6 *b*.

$$24m_0 = 15d_0 + 7(d_{11} + d_{12} + d_{13}) + 3(d_{21} + \ldots + d_{26}) + 2(d_{31} + d_{32} + d_{33}) \quad \text{...(22)}.$$

§ 8. GENERAL NETWORK. PROCEDURE FOR ADJUSTMENT

The foregoing analysis will have made quite clear the limitless possibilities of mathematical solution by means of correlate equations and multipliers suited to any cell of a network and its immediate surroundings. Interesting as such analysis is, its application to a practical problem of least-square adjustment must be governed by considerations of the accuracy justified in the particular survey, and the most economical method of executing the calculations involved. Adjustment involving elimination of the correlates of the first-remove cells on the lines of §§ 4 and 5, using equations (6) to (11), is a simple, reasonably rapid process, readily applicable to any cell in any network however complicated. When the network is homogeneous, i.e. when all the cells are polygons of the same species and regular in arrangement, the more rapid approximations discussed in §§ 6 and 7 may be used with advantage. Also when there are outstanding runs or chains of cells equations (16) to (19) are easy to apply and give very rapid approximations.

For general purposes, the procedure of §§ 4 and 5 is recommended as being simple, universally applicable and almost as rapid as any of the subsequent processes when account is taken of all the stages of the operation. As a test of this procedure, an adjustment made for a network of 56 Eötvös gravity stations may be cited. The observations were made in the course of a practical survey in Cumberland. The stations are shown as open circles in figure 7, where they are connected by broken-line links to form 80 triangles numbered 1 to 85, numbers 26 to 30 being omitted. It is evident that the network thus formed is typical of a large regional survey and that the procedure of linking could be adapted to any group of stations, however numerous. From the measured data of the gravity survey the increments in g were calculated for every link, and from these the excesses were derived for each triangle of the network. The excesses for the first ten triangles are tabulated in table 8 in



3
1
9
5
2
18
17
10
7
4
19
8
6
23
21
16
14
12
25
24
22
20
15
13
11
47
45
44
42
40
38
36
34
32
49
48
46
43
41
39
37
35
33
31
68
67
66
65
64
63
62
61
60
59
58
57
56
55
54
53
52
51
50
69
82
80
78
75
73
71
81
79
77
76
74
72
70
84
83
85

Figure 7.

Table 8

Δ	d'	$\Sigma_1^{\text{iv}} m$	d^{iv}
1	− 13	− 14	− 5
2	5	− 34	1
3	3	− 46	− 4
4	37	− 46	− 2
5	− 121	− 111	− 4
6	− 130	− 143	− 3
7	− 290	− 205	− 1
8	− 136	− 72	− 4
9	180	35	4
10	45	40	2

convenient units which were subsequently transformed into decimal fractions of a dyne. The excesses varied in sign and size, many exceeding 100 units and the largest being 346. Many of the actual link-increments exceeded 1000 units, and as these depend on measured gravity-gradients of which the accuracy rarely exceeds 2 to 3 per cent in practice, it is considered meticulous to obtain the adjusted values of the link-increments to nearer than 10 units. The procedure thus resolves itself into one of obtaining from the excesses the corresponding correlates to the nearest 10 units.

Table 9

N	Δ	+ m'	m' −	Δ''	+ m''	m'' −	+ m'''	m''' −	+ m^{iv}	m^{iv} −
8	1		39	3		15		21		6
				4		2		37		1
	2	5								
			34			17		58		7
			− 4			− 2		− 7		− 1
6	2	15		5		78		23		7
				6		115		14		10
	1		13							
	3	3								
	4	37								
		42				193		37		17
			+ 7			− 32		− 6		− 3
7	3	9		1		4		2		7
				4		2		37		1
	2	5		7		210	27			22
	5		121	9	66			31	5	
			107			150		43		25
			− 15			− 21		− 6		− 4
7	4	111		1		4		2		7
				3		15		21		6
	2	5		7		210	27			22
	6		130	12		28		12		8
			14			257		8		43
			− 2			− 37		− 1		− 6
6	5		363	2	7			32		6
				6		115		14		10
	3	3		8		83	20			11
	7		290	10	51			16	7	
	9	180								
			470			140		42		20
			− 78			− 23		− 7		− 3

To facilitate setting down the related first and second-remove correlates corresponding to each key correlate, it is convenient to replace every triangle in figure 7 by a correspondingly numbered dot, situated roughly at its centre of position, and to join these dots by lines representing contacts of adjacent triangles. A triangle is thus represented by a point from which radiates a number (one, two or three) of lines to each of its first-remove points, from which again outwards radiate lines to the second-remove points. Commencing at any one point it is easy for the eye to pick up the first and second-remove points in turn. These are tabulated on the working sheets, of which table 9 shows a typical example used for the first five points in order. The first column, headed N, is used for the common divisors obtained from formulae (9) and (10) by simply subtracting the number of first-remove points from 9 in each case, since in this network $n = 3$ and $n^2 = 9$ throughout.

The second column marked Δ contains the key-point number, followed after an interval of one line by the numbers of its first-remove points in order. The third column, marked $+\,m'-$, is used for computing m' from the excesses given in table 8 and equation (9). The excess for the key point is multiplied by 3 and set down opposite that point; the $+$ and $-$ columns are totalled and the aggregate sum divided by N from column 1. The result is m' for this key point. In the fourth column headed Δ'' are set down the numbers of the second-remove points in order. These are used to obtain m'', m''', m^{iv} in succession according to equation (10) by means of the subsequent columns headed $+\,m''-$, $+\,m'''-$, ..., and the values previously obtained in column m' for each second-remove point.

The procedure is thus to set down the key, first-remove and second-remove points in columns 2 and 4, then the values N in column 1; compute m' for every key point and use the values so obtained in column 5 to get m'' for each point; use these latter values to get m''', and these to get m^{iv}, and so on. The values actually obtained are shown under the respective columns in table 8. The approximations to m obtained by summation $m' + m'' + m''' + m^{\text{iv}}$ are next given. The whole process for 80 points took 15 hours, an average of just over a quarter of an hour for each of the 56 gravity stations.

The adjusted link-increment values are easily obtained from the calculated m's by using equation (1), and the adjusted gravity value of each station relative to any one taken as datum can then easily be derived, and the isogams can be drawn.

A check on the accuracy of reduction is obtained by computing the residual excess for each triangle. From equations (1) and (2) it is easy to see that the residual excess d' is given by the formula *d′*

$$d_r' = d_r + \Sigma m_x - 3m_r,$$

which ought to be zero if the values m are accurately computed. The actual residual excesses which remained when the calculation was stopped at m^{iv} are given in table 8, column d', and are seen to be below the agreed limit of error of 10 units.

531.787

A STUDY OF A SENSITIVE MANOMETER DUE TO PROFESSOR ALBERT GRIFFITHS

By P. C. VINCENT, M.Sc., Research Student, Birkbeck College

Communicated by Prof. Albert Griffiths, April 24, 1933

ABSTRACT. The manometer is analogous to a U-tube water manometer but the air is replaced by pure air-free water, and the water is replaced by an aqueous solution of uranine whose density differs from that of pure water. When the apparatus was made of glass, errors arose from the solution of the glass by water, which increased the density of the feeble uranine solution. The manometer functioned well when the apparatus was made of silica, which is almost insoluble in water. In order to test the working of the manometer, the pressures given directly by it were compared with those calculated from measured rates of flow along a capillary tube. As the ends of the manometer liquid become diffuse in the course of time, the rate of flow was measured by means of a coloured index, and as the index became considerably distorted a special method was devised for determining its position.

The difference of pressure measured varied in value from about 2 dyne/cm.^{2} to about 20 dyne/cm.^{2}

The average numerical difference between the direct manometer readings and the calculated readings is about 1 per cent of the absolute readings. The average difference taking the sign of the difference into account is about $\frac{1}{3}$ per cent.

---

§ 1. INTRODUCTION

The object of the work was to test the accuracy of a sensitive manometer designed by Prof. Albert Griffiths. The manometer has been tested with differences of pressure varying in value from about 2 dyne/cm.^{2} to about 20 dyne/cm.^{2} in a closed circuit containing water.

The design of the manometer will perhaps be easily understood if an analogy be made between it and the ordinary U-tube water manometer. The ordinary water manometer measures the difference between the pressure of the air on one side of the U tube and that of the air on the other side. Imagine the air to be replaced by pure air-free water, and the water to be replaced by an aqueous solution of uranine whose density differs by ρ from that of pure water.

Let h be the reading of the manometer, i.e., the difference in height in cm. between the upper extremities of the uranine solution; then the difference in pressure equals $g\rho h$ dyne/cm.^{2}

§ 2. DESCRIPTION OF MANOMETER

The manometer has placed behind it a black scale with white division marks, and the reading is made with the aid of a blue light. As the green fluorescence is plainly visible with very feeble solutions, there was a promise of a very sensitive manometer.

Obviously the two upright arms of the U tube must be at nearly the same temperature, otherwise the difference in density due to difference of temperature will mask the difference in density due to the solution of the uranine. By working in a thermostat room, and by surrounding the U tube with copper, the error due to difference of temperature was probably made negligibly small.

The apparatus was first made of glass, but unexpectedly the manometer was a complete failure. The hypothesis was made that the failure was due to the glass dissolving to relatively different extents in the water and solution in the different sides of the apparatus. Subsequent experiments proved this hypothesis to be correct.

Silica is almost insoluble in water and the glass was therefore replaced by silica. At first the silica apparatus gave very hopeful results; but in the course of time it gave results which at the lowest pressures were inconsistent to the order of 20 per cent. Ultimately this error was found to be due to a gradual diminution in the fluorescing power of the uranine solution, this diminution being caused by traces of nitric acid left in the apparatus after cleaning it. At the beginning of the research the various taps were in perfect order, and there were no channels in which traces of the injurious nitric acid could be retained. Possibly the trouble was due to the development of these channels. In the earlier experiments the usual lubricant employed was cerate of resin.

In the later experiments instead of working with absolutely pure water, water containing a trace of caustic soda was employed and the lubricant used was a solution of pure unvulcanized rubber in pure vaseline. Consistent results, presumably accurate to 1 or 2 per cent, were now obtained.

The manometer is diagrammatically represented in figure 1, and the complete apparatus is depicted diagrammatically in figure 2. *JLENFSH* suggest the U tube, *J* and *H* are the points between which there is a difference of pressure, *E* and *F* are three-way taps, *N* is an ordinary one-way tap. To introduce the manometer liquid the taps *E* and *F* are suitably arranged and a flow of the manometer liquid is passed from *E* to *F*. Further details of a necessarily complicated method of procedure are given in § 4.

The ends of the manometric liquid become fuzzy in course of time even when the pressure difference is constant. A method was therefore devised for obtaining with confidence the reading of a fuzzy end with a reasonable degree of accuracy (§ 8)

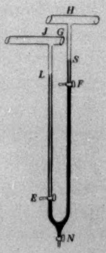


Figure 1.

Two methods have been adopted for the determination of the differences of pressure between two points in a capillary tube. The first method requires the employment under suitable conditions of a delicate manometer. The second involves a knowledge of both the resistance of the tube to a flow of water along it, and the rate of flow. The pressure varies as the product of the resistance into the rate of flow. Certain refinements in the procedure of the second method are described in the paper, and this method has been used as a check on the accuracy and serviceability of the first method. Comparisons suggest that both methods are reliable, to 1 or 2 per cent, and that the first method is likely to be quite as correct as the second.

The rate of flow of water in the second method was determined by the movement of a column of coloured index along a horizontal tube. This is called the index tube. The ends of the column become slightly fuzzy when the flow is very slow; they became very fuzzy under the conditions of the experiment, and as they were difficult to read, a special method was applied for determining the reading of the index (§ 12). The flow was developed by means of an electric current passing through a heating spiral, which surrounded one arm of a vertical U tube. For convenience this is called the vertical tube *OAP* of figure 2.

§ 3. THE METHOD AND THEORY OF TEST

The method and theory of testing the reliability of the manometer is as follows: (A) A definite, comparatively large pressure head of about 5 or 6 cm. of water is made to drive water through a horizontal capillary tube, and from the value of this head and of the rate of flow, the resistance of the capillary tube is calculated. In this experiment the manometer is not used. (B_1) A slow convective flow it made to take place along the same capillary tube, and from the rate of this flow and from the resistance determined by (A) the new pressure head is calculated, the head being proportional to the rate of flow. This flow is caused by a small electric heater. (B_2) The pressure head of the slow convective flow (B_1) is also measured directly by the uranine manometer. The pressure heads given by (B_1) and (B_2), being measurements of the same quantity, should substantially agree if the manometer functions properly.

P Let P be the pressure difference at the ends of the tube $JGDCBQH$, figure 2; and

V V the volume flow per second along the same tube under the pressure P.

K Then if the temperature be constant, $P = KV$, where K is a constant, called in this paper the *resistance* of the tube. If the temperature varies, then as K is a function of the temperature, and in accordance with Hoskings's* expression for

K_1 the manner in which the viscosity depends upon the temperature, K_1, the value

t_1 of K at t_1° C., is given by

$$K_1 = \frac{K_0}{1 + 0\cdot03445\,t_1 + 0\cdot000235\,t_1^2},$$

---

* Hoskings, *Phil. Mag.* **18**, 262 (1909).

where K_0 is the constant of the tube at 0° C. It follows that if K_2 be the corresponding value of K at t_2° C., then K_0, K_2

$$\frac{K_1}{K_2}=\frac{1+0\cdot03445\,t_2+0\cdot000235\,t_2^2}{1+0\cdot03445\,t_1+0\cdot000235\,t_1^2} \qquad \text{......(1).}$$

Thus if the value of K_1 be known for a temperature t_1° C., its value for a temperature t_2° C. can easily be calculated.

§ 4. APPARATUS USED FOR TEST, AND THE METHOD OF OBTAINING A SLOW FLOW ALONG THE CAPILLARY TUBE

For reasons already given and detailed later (see § 6) the apparatus used for testing the accuracy of the manometer was made of silica. The design of the apparatus is shown diagrammatically in figure 2.

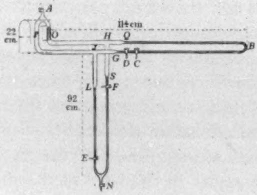


Figure 2.

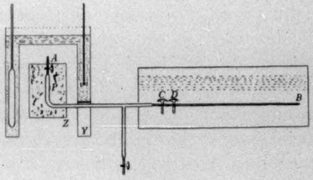


Figure 3.

The apparatus may be considered to consist of three parts: (1) the manometer tube *JLENFSH*; (2) the horizontal capillary or index tube *JGDCBQH*, on the right of the manometer, used for checking the accuracy of the manometer reading; and (3) the vertical tube *OAP*, on the left of the manometer, of the shape of an inverted U tube, and employed with the aid of an electric heater for obtaining the flow along the capillary tube.

The horizontal tube and the curved vertical tube to the left of the manometer are made up of wide bored tubing of diameter 0·5 cm. Round the vertical arm *O* is a heating spiral through which a feeble current is passed. The heating coil causes a convective flow upwards along *O*, down *P*, and round the horizontal circuit in the direction *JCBH*. The manometer liquid prevents a continuous flow round the manometer tube *JLENFSH*. The horizontal capillary or index tube to the right of the manometer is about 0·15 cm. in diameter. It contains two three-way taps *C* and *D*, by means of which a coloured index of uranine solution is introduced. The rate of movement of this index, under the influence of the convective flow, measures the rate of flow along the index tube. The manometer tube is about 0·2 cm. in diameter. The three-way taps *F* and *E* serve for the introduction of the manometric liquid.

Cleaning the apparatus. Before an experiment or a series of experiments the apparatus is cleaned with dilute nitric acid and a solution of sodium hydroxide, and finally distilled water is allowed to flow freely through it. The neglect, at one period of the research, to neutralize the nitric acid was a most costly mistake. In course of time a small trace of acid diminishes the fluorescence of a uranine solution in such a way as to vitiate the accuracy of the manometer, especially when weak solutions are employed. A long series of observations was ruined in this way.

Filling the apparatus. It might appear at first thought that the filling of the apparatus would be easy, but in practice the operation is difficult and tedious, because no glass or silica taps can be relied upon to withstand a pressure of water after they have been frequently used. A channel always forms on the inside of the barrel of the tap. This channel on the barrel of a three-way tap is particularly troublesome; for when the tap is turned so that there is communication from one side of the tap to the other, the channel allows water to leak from the inside of the apparatus to the open air, or vice versa. To prevent this, the outlet tubes of the three-way taps were sealed with indiarubber caps ("policemen" as they are called in the trade). The fitting of the cap is an art; if the cap is first filled with water and forced over the outlet tube, as water is almost incompressible, it is very difficult to prevent the water in the tap from forcing a way through the channel of the tap into the inside of the apparatus. The three-way tap or stop-cock used was of an ordinary type. The bores of the silica tubing on either side of the tap were in the same straight line, and thus when communication was made between the two sides of the tap, the bore of the plug was in a straight line with the manometer tube. A curved passage in a plane at right angles to the bore of the plug provided an outlet to the bottom of the plug.

When certain parts of the apparatus had to be filled, it was arranged that the water should run from one supply vessel to a receiver vessel; and care was taken that the level of the water or solution should be only slightly lower in the receiving vessel than in the supply vessel. A schedule of operations was drawn up covering a dozen sheets of foolscap. This schedule is not inflicted on the reader.

The apparatus is filled by opening the upper tap A and applying to it a head of distilled water. By opening and closing the lower tap N, and by manipulating the taps F, E, C and D, the whole apparatus can be washed through and filled with air-free distilled water. Water from the same containing-vessel is used to fill and wash the apparatus and to make up the manometer solution. It was found necessary when dealing with very dilute manometer liquids to add 5 cm.^{3} of a 10 per cent solution of sodium hydroxide to the water in the containing vessel, that is, to the water used in filling the apparatus, and making up the manometer solution. The containing-vessel has a capacity of 10 litres, and thus the concentration is 0·00005 gm. of sodium hydroxide per cm.^{3}

Introducing the manometer liquid. The manometer liquid is a weak solution of uranine of known density relative to water. The part ENF of the manometer tube is emptied of water and a head of the manometer liquid is applied to the tap N. The one-way tap N and the three-way tap F are then so arranged that the uranine solution flows in at N and out at F. No solution goes above F. Tap F is then closed and tap E is so adjusted that the solution passes in at N and out at E.

A sufficient quantity of uranine solution is passed through the manometer to ensure that there shall be no dilution of the solution by the residue of distilled water that previously filled the manometer tube. The tap *N* is closed, and the taps *F* and *E* are so turned that they shut off the manometer tube and only communicate with the upper index tube. By using the head of distilled water attached to the tap *A*, the exit bore of the tap *F* can be washed clean of the manometer liquid. The exits of the taps are sealed with rubber caps; this sealing is of vital importance. The taps *F* and *E* now separate the upper horizontal circuit containing distilled water from the manometer tube containing a weak solution of uranine, so the upper tap *A* may be left open and in communication with a reservoir of distilled water and yet leave the manometer liquid undisturbed. This allows the effects due to temperature, etc. to settle down before observations are made. The exit tap *N* is closed with a rubber cap and finally sealed with mercury, whilst throughout an experiment the tap *A* is left in communication with the reservoir of distilled water.

Introducing the index. The index, a column of uranine solution, is introduced into the index tube by means of the three-way taps *C* and *D*. The solution flows in at the port of *C*, up the vertical bore of the tap, along the capillary tube *CD*, and out at the port of *D*. The uranine supply is cut off and the taps *C* and *D* are turned through 90°, so that an uninterrupted flow can take place along the index tube. After the head of the index has travelled far enough along the tube, the length of the index can be shortened at will by washing through with distilled water from *C* to *D*.

The vertical U *tube and heating coil.* The two arms of the vertical tube *OAP* are embedded in asbestos wool. The vertical tube, copper block* and asbestos wool are enclosed in a copper cylinder *Z*, around which a water-jacket *Y* is placed which completely envelops it. The water within the jacket is electrically heated and stirred, and maintained at a constant temperature by a delicate thermostat control not indicated in figure 3.

The elimination of irregularities of temperature. All parts of the apparatus excepting the index tube, which is immersed in a water bath, are enclosed in copper shields.

The reading-scales. Beneath the horizontal index tube and behind the manometer tube are placed black centimetre scales lined out with white. The index scale is made water-proof as it is immersed in a tank of water. The manometer scale is marked out on a strip of sheet copper, which has been blackened with ammonium sulphide. Under the conditions of the experiment scales consisting of white lines on a black background are preferable to ordinary scales.

The situation of the index tube. The index tube is immersed in water contained in a large galvanized iron tank. The water in the tank can be stirred by an electric stirrer. Cooling due to the evaporation of the water in the tank is checked by covering the water with a wooden float that has been soaked in paraffin wax. Mercury thermometers are placed vertically in the tank.

---

* A block of copper measuring 8 × 4 × 1 cm. is placed about 1 cm. from the heating coil. This is introduced to increase the speed of attainment of a steady temperature-gradient between the two vertical arms. The same effect can probably be attained by placing the two vertical arms closer together.

The heating current. The heating current through the coil, figure 2, is obtained from two accumulators, and is controlled by a 130-ohm variable rheostat. The current is measured on a millivoltmeter placed across the terminals of a 4-ohm shunt. The resistance of the heating-coil is about 113 ohms. The current required to maintain a pressure head measurable by the manometer, and of the order of 3 or 4 dyne/cm.^{2} was determined by a series of preliminary experiments and was found to be about 24 mA.

§ 5. EFFECT OF IRREGULARITIES IN TEMPERATURE

The current required to maintain a constant manometer difference is found to depend upon the temperature of the water-jacket enclosing the heating portion of the apparatus. The main reason for this is undoubtedly the fact that the coefficient of cubical expansion of water varies so considerably with change of temperature. A numerical example will make this clear. It may be mentioned that in a certain experiment it was estimated that the difference of temperature between the two arms of the vertical heating tube was 1·5° C. Let the hypothesis be made that the difference in temperature between the two arms of the vertical heating tube is independent of the temperature of the enclosure; in the case of the apparatus under consideration this is approximately true. Consider the case in which the temperature of one arm is 20·5° C., and the temperature of the other arm is 22·0° C., the difference of density as given by ordinary standard tables is 0·000329 gm./cm.^{3} Now consider the case in which each arm is 1° higher in temperature, the temperature of one arm being 21·5° C. and the temperature of the other being 23·0° C.; the difference of density is now 0·000344 gm./cm.^{3} Thus an increase of 1° in the average temperature of the vertical heating tube increases the driving head by 15 parts in 329, that is, by $4\frac{1}{2}$ per cent, the current being constant.

§ 6. PRELIMINARY EXPERIMENTS WITH GLASS APPARATUS

Originally the manometer was made of glass and formed part of a glass apparatus, which was similar in design to the silica apparatus shown in figure 2. Although in the experimental work with the glass apparatus the flow along the index tube was normal—constant for a steady heating current and increasing with an increase of current—yet the manometer gave readings which were altogether unexpected. To simplify matters, and in the hope of determining the cause of the remarkable readings, it was decided to experiment without the heating-current.

Experiments without the heating-current. In the first experiment the manometer solution was introduced as shown in figure 1, and the solution flowed considerably past the equilibrium position, i.e., the position where the extremities of the uranine columns are level. Thinking that a mistake had been made, the apparatus was emptied and a new manometer solution was introduced. This time the difference between the levels of the uranine columns was at first + 63 cm.; it then dropped to zero and later became − 27 cm.; it then came back to zero and rose ultimately to + 48 cm. This experiment was also stopped whilst the movement was in progress. Tables of solubility of glass were consulted and it seemed quite reasonable to suppose that the odd results were due to the glass from the inner surface of the tube dissolving in the water and masking the action expected from the density difference between the water and the uranine solution.

The first experiment can be explained by assuming that the glass of the tube *FN*, figure 1, dissolved more rapidly per cubic centimetre of water than the glass of the tube *EL*. An explanation of the second experiment is not so simple. It can be obtained by assuming that the water in the horizontal part of the apparatus near the top of the tube *ELJ* dissolved glass fairly abundantly, and that at a certain moment a flow was engendered down the tube *JLE* and maintained by a supply of comparatively dense solution from the horizontal tube *JG*. A third experiment gave similar results to the second, and a fourth experiment gave similar results to the first.

To simplify the conditions still more, the manometer was separated from the horizontal part of the apparatus, and its upper ends were connected by an inverted U tube. In four successive experiments there was a flow consistent with the hypothesis that the water became denser in the arm *FN* than in the arm *EL*, figure 1. By turning the manometer through 180° about a vertical axis midway between the two tubes, it was proved that the effect observed was not due to a difference of temperature.

Results. In the first experiment under the simplified conditions there was the expected fall of the manometer due to the initial head of uranine solution, but the movement continued until the uranine solution was 4 cm. higher in the arm *EL* than in the arm *FN*. In the second experiment a similar movement took place until the difference was 10 cm. The difference was still increasing; and to test whether it was due to spatial inequality of temperature the apparatus was then turned through 180° about a vertical axis midway between the tubes. The movement continued in the same direction, and the difference in level was ultimately 16·5 cm.

The strength of the uranine solution in these experiments was 0·125 gm./litre, and to increase the sensitivity of the apparatus it was reduced to 0·0125 gm./litre.

In the third experiment there was a movement of 120 cm. down the arm *FN* and up the arm *EL*, the uranine solution being at the top of the apparatus at the conclusion of the observations. In the fourth experiment the uranine solution fell in the arm *FN* and rose in the arm *EL* until there was a difference of 77·5 cm. between its extremities.

The movement in each experiment was in the direction expected from the initial head of uranine solution, but greater than the head of uranine solution would account for, and it suggested a greater solubility of the glass in the tube *FN* than in the tube *EL*.

Experiments with tubes of the same material but of different diameters. Since the ratio of the volume of a cylindrical tube to the area of its inner curved surface varies directly as the radius, it follows that the narrower the tube the greater per cm.^{3} will be the rate of solution of the glass in the water within the tube; and if the manometer arms are of the same material but of different diameters, the flow should be down the narrower tube. This is exactly what did take place with a specially constructed piece of apparatus. The U tube and the manometer were separated and the ends of the manometer tube were connected by an elongated U tube, about 50 cm. long, one tube of which was 5 mm. and the other 2 mm. in diameter.

In the first experiment there was a movement of 93 cm. up the side of the wide tube. Many additional experiments which it is impossible to describe briefly were performed, and all the results obtained suggest that the rate of increase in the density of the water in the narrow glass tube is greater than the rate of increase in the wide tube.

§ 7. THE DENSITY OF THE MANOMETER SOLUTION

The method used in the determination of the difference between the density of the manometer fluid, a weak solution of uranine, and the density of pure water at the same temperature, was that of finding the change in weight of a sinker, approximately 1152 cm.^{3} in volume, when suspended in water and when suspended in a solution of uranine of known concentration, the weight of the sinker in air being known. The density difference was assumed to be proportional to the concentration*. From the determined density difference of a known concentration the density difference of a weak concentration was calculated.

The water and solution were well stirred between the weighings. The temperature was observed and allowance was made for changes in weight due to changes in temperature. As the temperature changes make the determination of the density difference difficult, it is important to keep the temperature of the liquid in which the sinker is immersed as uniform as possible; to do this the vessel which contained first the pure water and afterwards the uranine solution was surrounded by a water bath situated in a box lined with cork dust. To prevent cooling by evaporation, the surface of the liquid containing the sinker was covered with a layer of B.P. paraffin, and the temperature of this liquid could be maintained still more constant by the careful addition of warm water to the water-bath enclosure.

The results of the experiment of July 1931 will indicate the method. As speed was important the method of swings was used in the weighings, the sensitivity of the balance being 1·5 divisions per milligram. As the temperatures of the initial and final weighings were different, the weights were reduced to a standard temperature. The change in weight of the immersed sinker corresponding to a change of temperature was found to be 0·21 gm./° C., measured on a Beckmann thermometer.

---

* A. and C. H. Griffiths, *Proc. Phys. Soc.* **33**, 231 (1921).

The weight of the sinker immersed in water was ...	33·96 gm.
The weight of the sinker immersed in uranine solution (allowing for corrections) was...	33·2295 gm.
The loss of weight of the sinker was	0·7305 gm.
The volume of the sinker was	1151·8 cm.³
The volume of the solution in which the sinker was immersed was	12·5 litres
The weight of commercial uranine used in solution was	15·0 gm.

From the above results the density difference between a solution of uranine of concentration 1 gm./litre and pure water was found to be 0·0005283 gm./cm.³ at 20° C. This value was probably correct to the third significant figure. Determinations of the density difference between the manometer liquid and water were made for each sample of uranine used; this difference was found to depend upon the sample. The calculated density difference due to a concentration of 1 gm./litre was as follows:

Experiment	Uranine	Density difference
July 1931	Commercial	0·0005283 gm./cm.³
August 1932	Pure	0·0004196 gm./cm.³

Commercial uranine from the same sample, that had been carefully kept in a tightly corked bottle, and from which the density-difference determinations had been made, was used throughout the first series of experiments. Pure uranine from the same sample, that had been kept in a tightly corked bottle, and from which the second density-difference determinations were made, was used throughout the second series of experiments.

The influence of temperature on the difference between the density of the manometer liquid and that of water.

Let d_1 be the density of water at t_1° C.; d_1, t_1°
D_1 the density of the solution at t_1° C.; D_1
v_1 the specific volume of water at t_1° C.; v_1
V_1 the specific volume of the solution at t_1° C.; V_1
d_2, D_2, v_2, V_2 be the corresponding quantities at t_2° C.; d_2, D_2, v_2
and let t_2 be taken as less than t_1. V_2, t_2°

Insomuch that a weak solution must expand for a change of temperature by nearly the same amount as pure water, it is clear that

$$v_1/V_1 = v_2/V_2 \quad \text{and} \quad D_1/d_1 = D_2/d_2, \quad \text{whence} \quad (D_2 - d_2) = (D_1 - d_1)\, d_2/d_1.$$

If ρ_2 is the difference of density between the weak uranine solution and the water at a temperature t_2, and ρ_1 is the corresponding density difference at t_1, then, ρ_2 ρ_1

$$\rho_2 = \rho_1\, d_2/d_1.$$

In the experiments the ratio of d_2 to d_1 was little different from unity. Perhaps the point will be made clearer if we assume an approximate coefficient of expansion y of water in the neighbourhood of 20° C., the temperature of the manometer. y

Let $y = 0{\cdot}0002$, then

$$d_2/d_1 = v_1/v_2 = 1 + (t_1 - t_2)\,y.$$

If $(t_1 - t_2) = 2°$ C., an extreme difference of temperature for the experimental work, then

$$d_2/d_1 = 1{\cdot}0004 \text{ approximately.}$$

Thus $d_2 = 1{\cdot}0004\,d_1$, and if ρ_2 be taken equal to ρ_1 the error is less than $\frac{1}{20}$ per cent.

§ 8. A METHOD OF DETERMINING THE MANOMETER LEVELS

The uranine solution in the manometer was illuminated by a blue lamp. There is no sharp surface of separation between the uranine solution and the water above it. The uranine diffuses into the water and there is a centimetre or more where the uranine is gradually merging into the pure water. Both heads of the manometer column have substantially the same appearance, and it is possible to take readings of corresponding points; the difference between these readings should give the true manometer head. In practice the method proves difficult, and a method was devised which ensured both accuracy and ease, and gave a reading based on a great number of independent observations.

Figure 4.

A series of capillary tubes, figure 4, of the same diameter as the manometer tube, was filled with uranine solutions of graded concentrations. The uranine solution in tube 1 was of the same strength as the strongest manometer solution. The comparative concentrations of the other members of the series are detailed in Table 1.

Table 1

Tube	Strength	Tube	Strength	Tube	Strength
1	1·0	8	0·3	E	0·05
2	0·9	9	0·2	F	0·04
3	0·8	10	0·1	G	0·03
4	0·7	A	0·09	H	0·02
5	0·6	B	0·08	L	0·01
6	0·5	C	0·07		
7	0·4	D	0·06		

Each concentration tube was placed in turn against that part of the manometer where the uranine solution is slowly diffusing into the water above it, and by means of the blue lamp a series of positions of corresponding uranine concentrations was found upon the black manometer scale. A table of these readings and of the corresponding concentrations of the manometer solution, as indicated by the concentration-tubes, was made. An example of a series of readings of the same manometer level taken by independent observers by the concentration-tube method is detailed in table 2.

Table 2. Manometer readings and concentrations

Tube	Strength	Observer A	Observer A	Observer B	Observer B
		Level 1	Level 2	Level 1	Level 2
8	0·30	30·0	30·0	31·2	31·2
9	0·20	31·0	31·0	32·2	32·2
10	0·10	33·3	33·5	33·7	33·5
A	0·09	33·3	33·5	33·5	33·5
B	0·08	33·5	33·7	33·5	34·0
C	0·07	33·8	34·0	34·0	34·0
D	0·06	33·9	34·1	34·0	34·5
E	0·05	34·3	34·4	34·5	34·5
F	0·04	34·6	34·7	—	—
G	0·03	35·2	35·0	35·0	35·0
H	0·02	35·8	35·5	—	—
L	0·01	37·5	37·0	36·5	36·5
True levels		31·76	31·74	32·47	32·42
Difference		− 0·02		− 0·05	

Method of obtaining the true manometer level from a series of observations. Let C_0 be the maximum concentration of the manometer liquid, and consider any length dh of the diffused manometer extremity at which the concentration is C, then

C_0
h, C

$$Cdh/C_0$$

is the equivalent length of a manometer element at full strength, i.e., at concentration C_0.

Thus the equivalent length at full strength to the manometer column above a point whose reading is h_1 is

$$\int_{h_1}^{\infty} \frac{Cdh}{C_0};$$

or, if h_2 be the point at which the uranine is present in the manometer liquid in negligible amount, and if h_1 be a reading at which the concentration is C_0, then the true reading of the manometer is

h_2
h_1

$$\int_{h_1}^{h_2} \frac{Cdh}{C_0}.$$

The integration is performed with the aid of a graph and squared paper.

§ 9. THE INITIAL MANOMETER LEVEL

When experiments were made with the glass apparatus, it was found that even when no current was operating the levels of the manometer extremities differed considerably. It was important therefore to be sure that in the case of the silica apparatus there was no initial manometer head, that is, that the extremities of the manometer solution were at the same level when the current had been cut off and the manometer had been allowed to come to an equilibrium position. This was particularly important in the case of the very dilute manometer liquids.

The apparatus was washed and filled with distilled water, which in the case of the dilute manometer solutions contained a trace of sodium hydroxide. A current was put on for about twelve hours, sufficient to keep the manometer liquid between the limits of the taps *F* and *E* when these taps were open to the manometer movement. During the twelve hours, however, the taps *F* and *E* were turned so that the manometer was cut off from the effect of the density difference due to the heating current. At the expiration of the twelve hours the taps *F* and *E* were turned so as to bring the density difference into action upon the manometer. At the same time the current was lowered, usually in one stage, but in the case of the very dilute manometer solution in seven stages of one and a half hours each. A slow movement of the manometer has the advantages that the extremities are short, symmetrical, and less diffuse. As a result of lowering the current to zero the manometer fell until its extremities were at the same height in the two arms. The positions of the manometer levels were found by the concentration-tube method already described.

The results of various tests with manometer solutions of different concentrations are detailed in table 3. The average difference is 0·06 cm. The manometer was generally used with a difference of level of about 50 cm.

Table 3

Date 1931	Manometer strength (gm./litre)	Manometer level left	Manometer level right	Difference (cm.)	Observer	Drop of current (stages)
July 1	One	33·66	33·60	+ 0·06	A	One
,, 1	One	32·27	32·29	− 0·02	B	One
,, 1	One	32·97	32·97	− 0·00	A	One
,, 29	0·4	31·21	31·44	− 0·23	B	One
,, 31	0·4	33·13	33·23	− 0·10	A	One
Aug. 2	0·4	31·76	31·74	+ 0·02	A	One
,, 2	0·4	32·47	32·42	+ 0·05	C	One
,, 2	0·4	31·73	31·91	− 0·18	B	One
,, 6	0·2	31·79	31·70	+ 0·09	A	One
,, 8	0·2	31·69	31·76	− 0·07	A	One
Nov. 11	0·125	32·15	32·27	− 0·12	A	Seven stages each 1½ hours
,, 11	0·125	32·35	32·53	− 0·18	A	

§ 10. RAPID-FLOW EXPERIMENTS*

t_1 Let t_1 be the temperature of the rapid flow experiments;
P_1 P_1 the pressure in dynes/cm.² at t_1° C.;
V_1 V_1 the volume flow cm.³/sec. at t_1° C.; and
K_1 K_1 the resistance of the index tube (the value of K) at t_1° C.

Then

$$P_1 = K_1 V_1.$$

P_1 and V_1 are measured directly, and from their values K_1 is found.

---

* See § 3.

The measurement of K_1, the resistance of the index tube. The resistance of the index tube was measured directly by means of a known pressure head and a measured flow. The tube was separated from the apparatus at points between *JG* and *HQ*, see figure 2. This tube *JDCBQH* had a bore of such magnitude, that in order to make the energy correction negligibly small it was found advisable to have a head as small as 5 or 6 cm. of water.

X and *Y*, figure 5, are glass pneumatic troughs about 30 cm. in diameter, in the sides of which holes have been bored in order to provide connection with the tube *JCDBQH*. The water in each trough was covered with a layer of medicinal paraffin oil. This prevents evaporation and thus makes for reliability in an estimation of a change of volume by means of the change in weight, and further, the absence of evaporation makes the temperature more constant. The two arms *PQ* and *RS* were attached to a vertical slider actuated by a screw, and the ends *Q* and *S* were provided with needle points. White paper was placed at the bottom of each trough and light was cast on the trough from above. When the arms *PQ* and *RS* were lowered a characteristic bright spot was formed on the paper at the moment of contact of the needle point with the surface of the paraffin oil. The readings of the same level were often absolutely the same, and they very rarely varied by as much as 0·002 mm. The correction to be applied because the needle point of *Q* was not at the same height as that of *S*, and also for the fact that there were not necessarily layers of the same thickness of paraffin oil in each trough, was made by connecting the troughs by a wide tube so as to produce equilibrium between the two troughs, before making appropriate measurements. The volume of the liquid which passed from *Y* to *X* was determined by weighing *X* on a strong balance before and after the flow.

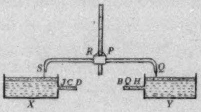


Figure 5. Diagrammatic sketch of the apparatus.

In a typical experiment the total flow of water was 325 gm., the rate of flow along the capillary tube was 2·7 cm. per minute, the kinetic energy correction was less than 0·1 per cent, and the correction for the auxiliary tubes connecting the troughs to the capillary tubes was less than 0·3 per cent. Three determinations of *K* were made, two with a flow in one direction and one with a flow in the other direction; the values of *K* were reduced to a standard temperature of 20° C., and the average value of K_1 was taken as correct.

		Value of K_1
Results.	1st experiment, direct flow	127652
	2nd experiment, direct flow	127204
	3rd experiment, reverse flow	127619
	Average	127492

K_t The average value of K_1 at 20° C. was taken to be 127500. The value of K_t, the resistance at t° C., is given by

$$K_t = 127500 \times \frac{1 + 0{\cdot}03445 \times 20 + 0{\cdot}000235 \times 20^2}{1 + 0{\cdot}03445 \times t + 0{\cdot}000235 \times t^2}$$

$$= \frac{227300}{1 + 0{\cdot}03445 \times t + 0{\cdot}000235 \times t^2}.$$

Experiment of December 27, 1930.

h_0 h_0, the initial head was 6·517 cm.;
h_1 h_1, the final head was 5·520 cm.;
M M, the total flow was 325·7 gm.;
t t, the temperature of the water was 19·46° C.;
ρ ρ, the density of the water was 0·998 gm./cm.^{3};
Q Q, the total flow was M/ρ cm.^{3};
T T, the time of total flow was 7200 sec.;
a a, the radius of the index tube was 0·0735 cm.

The equation for K, uncorrected for the kinetic energy of flow, is

$$K = \frac{\rho g (h_0 - h_1)}{V \log (h_0/h_1)}.$$

The value of K, corrected for the kinetic energy of flow, is given very approximately by

$$K = \frac{1}{v}\left[\frac{\rho g (h_0 - h_1)}{\log_e (h_0/h_1)} - \frac{v^2 \rho}{a^4 \pi^2}\right].$$

Experiment of December 27, 1930.

K uncorrected was 129800 at 19·46° C. The kinetic energy correction given by $\rho V/\pi^2 a^4$ was 156; this is relatively small. The corrected value of K was then 129644. K reduced to a standard temperature of 20° C. became 127944. The correction for the resistance of the auxiliary tubes was 325, obtained from the expression $8l/\pi r^4$, where r is 0·26 cm. and l is 56 cm.

The final value of K was 127619.

§ 11. SLOW-FLOW EXPERIMENT

Let t_2, P_2, V_2 and K_2 be the corresponding values of t_1, P_1, V_1 and K_1 for the slow-flow experiments, then

$$P_2 = K_2 V_2.$$

Since the evidence* is in favour of the viscosity having the same value at low rates of shear as at high rates, we may by using equation (1) write this as follows:

$$P_2 = K_1 V_2 \frac{1 + 0{\cdot}03445 t_1 + 0{\cdot}000235 t_1^2}{1 + 0{\cdot}03445 t_2 + 0{\cdot}000235 t_2^2}$$

or

$$P_2 = V_2 \frac{227300}{1 + 0{\cdot}03445 t_2 + 0{\cdot}000235 t_2^2} \qquad \ldots\ldots(2).$$

---

* A. and C. H. Griffiths, *Proc. Phys. Soc.* **33**, 231 (1921).

This equation determines P_2, for the value of K_1 has been determined experimentally, and V_2 and t_2 are measured directly.

Method of making a slow-flow experiment. The apparatus is cleaned and filled. After the filling the manometer taps are so turned that they separate the horizontal circuit from the manometer. The tap A, figure 2, is left open and in communication with a reservoir of distilled water. A pressure head is used so that the extremities of the manometer column are well out of the taps. A current of sufficient strength to maintain this pressure head is passed through the heating coil; this current is determined by a series of preliminary experiments. The water baths of the index tube and vertical tube may be gently stirred, and thermometers are placed vertically in these baths. A thermometer is also placed close to the centre of the manometer scale. The index taps C and D are turned so as to prevent any movement of the index. The apparatus is then left about twelve hours to ensure steady conditions.

At the close of the waiting period the manometer taps are turned so that the manometer difference adjusts itself to the pressure arising from the convective flow due to the heating current. When the manometer reaches a steady state, the index taps C and D are turned so as to allow a movement of the index along the horizontal tube. The exact time of opening these taps is noted.

The apparatus is now so arranged that the manometer liquid shall register any difference of pressure arising out of a density difference within the arms of the vertical tube due to the heating effect of the current, and the movement of the index should indicate the rate of movement of the convective flow along the horizontal tube.

The whole apparatus is in a double-walled room. The position of the index and the manometer levels, the temperatures of the water baths of the horizontal and vertical tubes, and the temperature of the manometer are read at regular intervals. From these, the volume flow per second through the index tube, the pressure as indicated by the difference in manometer levels, and the temperature of the water in the index tube are known. The current strength is checked at regular intervals. The position of the index and of the manometer levels is judged by the methods already explained.

§ 12. THE READING OF THE INDEX

The positions of equal colour-intensity in the index and the corresponding concentrations in the graded concentration tubes are noted. A figure is then drawn on squared paper in which the readings of the positions of the tubes as abscissae are plotted against the concentrations as ordinates. A figure $ABCDE$, figure 6, is thus obtained. The figure is cut out and its centre of gravity obtained by balancing. The ordinate of the centre of gravity is taken as the reading of the index.

An account of the reasons why Prof. Griffiths suggested the centre-of-gravity method may not be out of place. Let us, in the first place, suppose that there is a coloured index of uranine solution in an infinitely long horizontal tube of uniform bore containing water at rest. Let it be assumed that the only cause of the elongation of the index is diffusion, and that at a given moment the density of the solution is uniform over a cross-section at right angles to the length of the tube. For purposes of mathematical analysis the coloured index may be imagined to consist of an indefinitely large number of small elements bounded by vertical planes normal to the axis of the tube. The uranine in each element may be supposed to diffuse symmetrically, and therefore there can be no change, arising from diffusion, in the position of the centre of gravity of the uranine originally in the element. It follows then that as the position of the centre of gravity of each element is unaffected by diffusion, the position of the centre of gravity of the whole index is unaffected by diffusion, i.e. the centre of gravity of the uranine index remains exactly in the same position and is independent of diffusion.

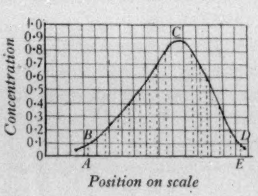


Figure 6.

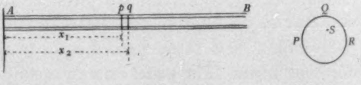


Figure 7.

Now let us consider the case when the water is not at rest. An element of the uranine now experiences a movement due to two causes, one being the movement of the water in a given direction, and the other being due to diffusion, or molecular movement.

Let AB represent the horizontal tube along which the steady flow of water is taking place, and let p, q indicate two adjacent vertical planes normal to the
x_2, x_1 direction of flow, at a distance $(x_2 - x_1)$ apart. Suppose the bore of the horizontal tube to be so small that in spite of the flow the density may be considered uniform over any cross-section such as p. Let PQR represent the cross-section of the bore,
a and da an element of area at S.

c_1 Let c_1 be the concentration at the cross-section p;
k k the coefficient of diffusion of the solution;
v v the normal component of the velocity of the flow at S, which is not constant over the cross-section.

t The quantity of uranine crossing the element da in time dt may be written

$$\left[\int vc_1 da - k\frac{dc_1}{dx}\int da\right] dt,$$

the integration being taken over the whole cross-sectional area. It is assumed that c_1 is uniform over the plane A, the intersection of p with the bore of the tube.

Then the quantity of uranine entering through p into the space between p and q equals

$$\left[c_1 \int v\,da - k\frac{dc_1}{dx}\int da\right] dt,$$

the integration being taken over the whole cross-section.

Let A be the area of the cross-section, and V the volume flow per second, then the quantity of uranine crossing p from left to right, the direction of the flow, may be written A, V

$$[c_1 V - kA\,dc_1/dx]\,dt.$$

Let U be the average velocity of the linear flow along the tube, U being defined as V/A; then the quantity of uranine entering through p into the space between p and q equals U

$$A\,[c_1 U - k\,dc_1/dx]\,dt.$$

The quantity of uranine crossing q from left to right in time dt equals

$$A\,[c_2 U - k\,\{dc_1/dx + (x_2 - x_1)\,d^2c_1/dx^2\}]\,dt.$$

The rate of increase of the quantity of uranine per unit time between p and q therefore equals

$$AU\,(c_2 - c_1) + Ak\,(x_2 - x_1)\,d^2c_1/dx^2.$$

That is, the rate of increase of uranine per unit volume per unit time in the element between the cross-sections p and q equals

$$\frac{AU\,(c_2 - c_1) + Ak\,(x_2 - x_1)\,d^2c_1/dx^2}{A\,(x_2 - x_1)},$$

that is

$$U\,dc/dx + k\,d^2c/dx^2,$$

or

$$\frac{dc}{dt} = U\frac{dc}{dx} + k\frac{d^2c}{dx^2}.$$

This equation proves that there is no necessity to know the character of the flow along the capillary, so long as it is steady and uniform. The flow may be of the parabolic type or may be any function of the position of S in PQR; in all cases the index varies in character in course of time, just as it would if the water moved through the tube with a constant velocity at all points in the tube.

A mental picture of the flow is obtained if we imagine the liquid to be replaced by a transparent solid rod moving along the tube. Now moving the rod will not appreciably affect the diffusion in relation to the rod, and the centre of gravity of the index will therefore remain in the same part of the rod; and thus if the rod move with velocity U, the centre of gravity will move at the same speed. It may be noted that there is no need for the index to be symmetrical.

So far we have only considered the elongation of the index as caused by diffusion. As a matter of fact the elongation of the index may be due to gravity. The movement due to gravity decreases with the increase in dilution, and also diminishes with a diminution in the radius of the capillary tube, as the effect of the viscosity of the water increases with the diminution in radius.

Thus when the diameter of the capillary tube is sufficiently small, or the concentration of the index solution sufficiently small, or, to be more general, some unknown function of the diameter, concentration, and concentration-gradient is sufficiently small, gravity may be neglected in comparison with diffusion.

A number of experiments have been performed which prove that a weakening in the concentration of the solution or a diminution in the diameter of a tube does actually make the effect due to gravity appreciably small.

To compare the effect of a combination of diffusion and gravity-convection with the effect due to diffusion alone, it is convenient to compare the transmission of uranine along a vertical tube originally containing water with that along a horizontal tube. It is quite easy to carry out rough experiments. In one series a Woulff's bottle was employed. To study the horizontal transmission two tubes were fixed in the horizontal necks, the Woulff's bottle was filled with water and the water was allowed to fill the tubes. The tubes were then sealed with indiarubber caps. The water in the Woulff's bottle was then replaced by uranine solution. A third tube was filled with water, one end being closed. The water stays in position even when the tube is held vertical with the opening downwards. It is thus easy to place the vertical tube in position with the lower end in the uranine solution.

A different apparatus has been used in which the transmission takes place down the tube. With a uranine solution of the same concentration as that used for the index, i.e. 0·25 gm./litre, and a tube of bore 1·5 mm., there was no substantial difference between the horizontal and vertical transmissions. With a uranine solution of concentration 5 gm./litre, and tubes of bore 1·5 mm., the transmission horizontally was distinctly bigger than the pure diffusion upwards. The transmission down the vertical tube was considerable. With a uranine solution of concentration 5 gm./litre, and tubes of bore 0·5 mm., the transmission vertically downwards was very much less than that down the tube of diameter 1·5 mm.; and the horizontal transmission was little different from the pure diffusion upwards. In practice, in the course of time, the gravity-effect automatically becomes relatively less important.

As has already been explained, the density of the uranine at various points is determined with the assistance of a series of graded proof tubes, as they may be called. Numerous readings are taken, and individual errors tend to average out. The method requires a long time for a complete reading. In practice the position of the index may be obtained to a fair degree of accuracy by taking the mean of readings in the neighbourhood of the points of inflexion of the graph, figure 6. It is not proper to take the mean of the whole number of readings, as this gives too much weight to the readings of the proof tubes filled with weak solutions. This method does not give the same position of the index as the centre-of-gravity method, but the difference between two positions of the index obtained by the two methods is roughly the same.

§ 13. INTERPRETATION OF THE EXPERIMENTAL RESULTS

To find for one complete experiment the average value of the manometer difference, the mean of two consecutive readings was multiplied by the time interval between the readings. These products were then totalled for the whole experiment and divided by the complete time interval between the first and last reading of the manometer. This value should give the average value of the manometer difference throughout the experiment. A corresponding method was adopted with the temperature-readings.

Experiment of February 6, 1932. The average value of the manometer difference measured directly was 49·17 cm.

The average temperature t_2 of flow was 21·2° C.

The average flow per second V_2 was 0·00002052 cm.^{3} The flow per second was obtained by taking the initial and final positions of the index on the calibration graph, and dividing the volume thus found by the total time.

Substituting in equation 2 the values of V_2 and t_2, we have

$$P_2 = 2{\cdot}54 \text{ dyne/cm.}^2$$

If we consider the equation

$$P_2 = hg\rho,$$

where h is the manometer difference in centimetres and ρ is the density difference between the uranine solution and the water in the manometer, i.e. 0·00005245 gm., then $h = 49{\cdot}3$ cm. **h, ρ**

As has been stated above, the manometer difference measured directly by the concentration tubes was 49·17 cm. Thus there is a difference between the measured and calculated manometer head of 0·2 cm.

The correction for the manometer movement. A correction has to be applied to the measurement of the manometer difference because of the slight movement of the manometer during an experiment.

Let r be the radius of the manometer tube, i.e. 0·0944 cm.; **r**
l the length of the manometer tube, i.e. 169 cm.; **l**
η the coefficient of viscosity of the manometer solution at the temperature of the manometer. This is substantially the same as that of pure water. **η**

For a manometer movement dh performed in time dt

$$V = A\,dh/2dt.$$

Then the difference of pressure between the two ends of the manometer at any moment, where h is the average measured manometer difference during the movement dh, equals

$$g\rho h + 4l\eta\, dh/r^2 dt.$$

The average pressure T over a time equals **T**

$$g\rho \int \frac{hdt}{T} + \left[\int \frac{4l\eta}{r^2} \frac{dh}{dt} dt \right] \frac{l}{T}.$$

If P be the corrected pressure in dynes, then **P**

$$P = (g\rho \times \text{average difference of manometer levels}) + \frac{4l\eta}{r^2} \int_{h_0}^{h_T} \frac{dh}{T},$$

h_0, h_T where h_0 is the initial and h_T the final manometer difference in time T.

$$P = g\rho h + \frac{4l\eta}{r^2}\frac{(h_T - h_0)}{T}$$

$$= (g\rho \times \text{average difference of manometer levels}) + \frac{4l\eta}{r^2}\frac{(h_T - h_0)}{T}.$$

The above proves that the corrected reading of the manometer equals the average difference of level plus $4l\eta/r^2$ multiplied by the average rate of change with respect to time of the manometer reading, however inconstant the rate of variation may be. Inasmuch as the correction is small, no great accuracy is required in the values of l and r.

As an example of the correction for the manometer movement consider the experiment of February 6, 1932.

The initial manometer difference was 49·20 cm.

The final manometer difference was 49·72 cm.

The change in manometer difference was + 0·52 cm.

The total time of flow T was 1080 minutes.

The temperature of the manometer was 21·8° C.

The coefficient of viscosity was 0·00963.

The density difference of the manometer solution was 0·00005245 gm./cm³.

If D be the correction in centimetres, then

$$D = 4l\eta\,(h_T - h_0)\,r^2/g\rho T.$$

Substituting the above values and changing the minutes to seconds, we obtain

$$D = 0{\cdot}12 \text{ cm. approximately.}$$

Therefore + 0·12 cm. has to be added to the average manometer difference of the experiment, i.e. 49·05 cm., to obtain the true manometer height; this equals 49·17 cm. The average correction for the manometer movement taken over the whole range of experiments was − 0·07 cm. This on an average manometer difference of 40 cm. is a correction of about 0·14 per cent.

Various density differences were experimented with, and the results were tabulated as in the following example:

Date. July 11, 1931. Time of flow 171·3 minutes.

Total flow 1·718 cm³. Rate of flow 1672×10^{-7} cm³/sec.

Mean temperature during flow 22·15° C.

a Measured difference a of manometer levels 38·92 cm.

b Calculated difference b of manometer levels 39·14 cm.

$a - b = -\,0{\cdot}22$ cm.

Current in quarter-milliamperes = 248. Density difference $\times 10^3$ = ·5283 gm./cm³.

c a expressed in dyne/cm² = c = 20·17.

d b expressed in dyne/cm² = d = 20·29.

$c - d = -\,0{\cdot}12$ dyne/cm².

§ 14. PRECAUTIONS WITH WEAK SOLUTIONS

It was found during an unfortunate period of work that with very dilute solutions of concentration-difference 0·00005 gm./cm.^{3}, the extremities of the uranine columns became fainter in the course of time, and to an unequal extent; and that when there was no heating current the levels did not come the same. This was found to arise from a definite diminution in the fluorescing power of the manometer solution, and was apparently due to the chemical action of traces of nitric acid left in the apparatus. The taps had become worn in the course of time, and there were the usual channels due to the turning of the plug in the barrel; thus there were many places where traces of acid could remain.

The trouble vanished when a trace of caustic soda was added to the water used in the experiments. At this stage, as an additional precaution, the taps were reground; also a lubricant made up of a solution of pure unvulcanized rubber in pure vaseline was used. This solution was most satisfactory both as a lubricant and as a seal.

During the preparation of an experiment, after the apparatus had been washed with dilute nitric acid, the manometer taps were removed, washed again with distilled water and dried, washed with a solution of sodium hydroxide, washed again with distilled water and dried, washed with methylated spirit and dried, and finally relubricated. The whole apparatus was in a double-walled thermostat room. In the case of the later experiments the electric stirrer was removed from the rectangular tank containing the horizontal capillary tube, in order to eliminate the possibility of vibrations affecting the results.

With these changes the experimental work proceeded as with the stronger manometric liquids. The thermostatic conditions of the room were relied upon to maintain the apparatus at a reasonably constant temperature, and to keep an even distribution of temperature throughout. As an example, during the experiment of March 26, the average room-temperature varied by 0·4° C., and the temperature of the tank containing the index tube varied by 0·15° C. The temperature of the water jacket surrounding the heating section of the apparatus varied by 0·07° C.

§ 15. SUMMARY OF RESULTS

Density difference (gm./cm.^{3})	Date, 1931	Measured manometer difference a (cm.)	Calculated manometer difference b (cm.)	Difference $a-b$ (cm.)	Average difference	Average difference %	a (dyne/cm.^{2})	b (dyne/cm.^{2})	$a-b$ (dyne/cm.^{2})	Difference %
0·0005283	July 11	38·92	39·14	− 0·22	− 0·3	− 0·78	20·17	20·29	− 0·12	− 0·59
	July 19	37·59	37·54	+ 0·05			19·47	19·45	+ 0·02	+ 0·10
	July 21	37·86	38·59	− 0·73			19·62	20·00	− 0·38	− 1·90
0·0002112	July 25	51·93	52·47	− 0·54	+ 0·013	+ 0·025	10·76	10·87	− 0·11	− 1·01
	July 28	51·34	51·77	− 0·43			10·64	10·73	− 0·09	− 0·84
	July 31	53·74	53·35	+ 0·39			11·13	11·05	+ 0·08	+ 0·72
	Aug. 1	52·86	52·77	+ 0·09			10·95	10·93	+ 0·02	+ 0·18
	Aug. 4	53·00	52·77	+ 0·23			10·98	10·93	+ 0·05	+ 0·46
	Aug. 8	53·24	52·90	+ 0·34			11·04	10·95	+ 0·09	+ 0·82
0·0001678	Aug. 15	47·91	48·48	− 0·57	+ 0·00	+ 0·00	7·89	7·98	− 0·09	− 1·13
	Sept. 12	48·83	48·17	+ 0·66			8·04	7·93	+ 0·11	+ 1·39
	Sept. 19	48·43	48·52	− 0·09			7·97	7·99	− 0·02	− 0·25
	1932									
0·0001049	Apr. 10	50·77	51·84	− 1·07	− 0·34	− 0·65	5·23	5·33	− 0·10	− 1·88
	Apr. 16	51·53	52·34	− 0·81			5·30	5·39	− 0·09	− 1·67
	Apr. 23	53·01	53·27	− 0·26			5·46	5·48	− 0·02	− 0·37
	Apr. 30	53·59	53·25	+ 0·34			5·52	5·48	+ 0·04	+ 0·73
	May 7	52·21	52·13	+ 0·08			5·37	5·31	+ 0·06	+ 1·13
0·00005245	Feb. 6	49·17	49·51	− 0·34	− 0·10	− 0·19	2·53	2·55	− 0·02	− 0·78
	Feb. 13	54·35	55·67	− 1·32			2·80	2·86	− 0·06	− 2·10
	Mar. 26	52·78	52·82	− 0·04			2·72	2·72	− 0·00	− 0·00
	Mar. 30	52·39	52·49	− 0·10			2·70	2·70	− 0·00	− 0·00
	May 15	54·68	53·55	+ 1·13			2·81	2·76	+ 0·05	+ 1·81
	May 21	52·72	52·67	+ 0·05			2·71	2·71	+ 0·00	+ 0·00
						Average − 0·30				Average − 0·27

§ 16. TESTS OF ACCURACY

The index tube was separated from the rest of the apparatus and a fine capillary tube was attached to one end, while the other end was connected to a head of water. By preliminary experiments the head of water and the fineness of the capillary tube were so adjusted that the flows of water through the capillary tube and index tube were approximately those of the slow-flow experiments. An index was introduced into the index tube, and its movement was measured by the centre-of-gravity method already explained in § 12 of this paper. The corresponding flow of water through the index tube was measured by dipping the free end of the capillary tubing into a weighed beaker of water, whose surface was covered with medicinal paraffin oil. The increase in the weight of the beaker and its contents gave the flow of water through the index tube in grams. From the linear movement of the index obtained by the method quoted above, the volume flow in cubic centimetres was obtained from the calibration graph. The flow as given by the movement of the index should, if the method be right, equal that given by the weighing.

The following results show that the measurements of the linear flow as described in this paper are correct to a fraction of 1 per cent.

Experiments ...	1	2	3	4	5	6	7	8	9	10
Pressure heads (cm.)	30·0	30·0	27·0	24·5	20·5	24·5	14·3	15·0	6·5	9·0
Linear flow (cm.)	96·29	61·95	80·0	88·85	88·5	92·45	88·52	90·0	83·95	81·6
Time (min.)	261	216	320	346	390	420	540	590	1300	1365
Speed (cm./hour)	22·14	17·2	15·0	15·5	12·9	13·2	9·84	9·14	3·9	3·59
Flow ($10^{-6} \times$ cm^3/min.)	6330	5139	4279	4422	3879	3788	2805	2625	1104	1023
Index flow *a* (gm.)	1·650	1·093	1·374	1·525	1·515	1·584	1·515	1·544	1·439	1·399
Flow by weighing *b* (gm.)	1·652	1·110	1·368	1·530	1·513	1·591	1·507	1·549	1·434	1·396
Percentage difference between *a* and *b*	− 0·12	− 0·60	+ 0·40	− 0·30	+ 0·17	− 0·44	+ 0·50	− 0·32	+ 0·30	+ 0·22

The average percentage difference between *a* and *b* is 0·34 per cent.

It ought to be mentioned that the taps were far from ideal: the bores of the taps were far from cylindrical in shape. In fact they were of conical shape near the barrel. The index had to travel through the wide spaces at the end of the bore and when it had emerged from the tube between the taps *C* and *D*, figure 2, it was very unsymmetrical, and was longer than it would have been if the taps had been perfect. Moreover, shortly after emerging from the tap, the index had to pass through an enlargement of the bore made in the sealing together of the parts of the apparatus. This still further increased the dissymmetry and the length of the index.

In order to test the accuracy with which the manometer could be read, experiments were made with a silica apparatus constructed according to the design suggested in figure 8. *A* is an ordinary tap, *B* and *C* are three-way taps of the same type as those used in the manometer. The length of the apparatus is about 30 cm., that is, the distance round the circuit is about 60 cm., and the bore of the tube is about 0·2 cm. The part of the apparatus below *B* and *C* was filled with a uranine solution and that above *B* with distilled water. It was hoped that on arranging the taps *B* and *C* so that a vertical flow could take place, the difference in level between the ends of the columns of uranine solution would gradually become zero and remain zero. This was the case with the comparatively strong solution of uranine, viz. 0·000250 gm./cm^3. The difference did become zero and remained at zero; but with very feeble solutions the results were of an unexpected character.

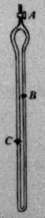


Figure 8.

The rate of movement of the ends of the columns in this latter case was not in accordance with the rate of movement as calculated from the dimensions of the apparatus, the viscosity of water, and the density of the uranine; and moreover the difference of level did not remain at zero after reaching zero, for when the difference of level was zero the columns were in movement, and the extremity of the left-hand column later became higher than that of the right, once by 2 cm. Then there was a slow reverse movement, and after two or three days the difference of level became zero.

The experiments suggest that when the feeble solutions were used in the manometer described in this paper, it would have been better to have had an interval of two or three days after filling the apparatus before making comparison between the pressure as deduced from the flow and that given by the manometer. In practice the interval was generally from 16 to 20 hours.

If it is possible to make further experiments, the hypothesis will be made that the anomalous results of the feeble solutions were due to small particles suspended in the water, and that these particles gradually subsided, or deposited themselves on the walls of the silica tube.

The apparatus was made with the assistance of a grant from the Waller Research Fund.

§ 17. ACKNOWLEDGMENT

Thanks are due to Dr Constance H. Griffiths, a fellow research student, who gave valuable help by her general interest in the progress of the work, and particularly by her assistance in the careful density difference determinations.

531.756.5 : 531.787

AN APPLICATION OF A NEW METHOD, DUE TO PROFESSOR ALBERT GRIFFITHS, OF DETERMINING A SMALL CHANGE IN THE DENSITY OF A LIQUID

By P. C. VINCENT, M.Sc., Research Student, Birkbeck College

Communicated by Prof. Albert Griffiths, April 24, 1933

ABSTRACT. The paper describes a manometer method for determining changes in the density of water due to prolonged contact with glass.

This paper is a continuation of a previous paper* and describes a rough measurement of the change in density of water which has been standing in glass tubes for days. It describes experiments which (*a*) support the hypothesis that the solution of the glass by water with a consequent increase in the density was responsible for the remarkable results obtained with the manometer made of glass tubing; (*b*) show that the density of water kept in a silica tube does not change appreciably in the course of weeks; and (*c*) enable the changes in density of samples of water which have been kept in contact with glass for various periods to be obtained.

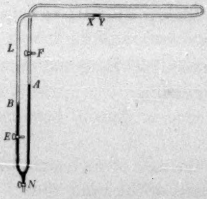


Figure 1.

For simplicity of explanation consider the apparatus modified as in figure 1. If the closed circuit be filled with liquid of uniform density, there will be no movement of the liquid; but if a denser liquid be introduced as indicated in the figure, and if the level *A* of the denser liquid be higher than the level *B*, a movement of the index *XY* will take place from left to right. If on the other hand *B* be at a higher level than *A*, the movement will be in the opposite direction.

By the virtual elimination of the parts *HOAPJ* of figure 2 of the prior paper, the apparatus depicted in figure 1 is obtained. In practice it was found advisable to introduce a length of indiarubber tubing provided with a screw clip into *HO* and also to introduce a similar length of tube into the part *PJ*.

---

* Page 808 of this issue.

Experiments A. (1) After the apparatus had been filled with pure water and had settled down, a new sample of pure water was introduced into the space *FNE*. As was expected there was no movement of the index. (2) Four times, water which had been in glass tubes of diameter approximately 0·2 cm. for periods varying from 4 to 29 days was introduced into *FNE*. In each case the index moved in the direction expected. (3) Twice, water which had been in glass tubes for periods of 8 and 31 days respectively was introduced into the tube at the three-way tap *E*, figure 1, so as to occupy the part of the tube *EL*. The index now moved in the opposite direction, i.e. in the direction expected. The details of the method employed are not given here.

Experiments B. (1) Water which had been left in a silica tube of diameter 0·2 cm. for 27 days was introduced into the space *FNE*. There was a negligible movement of the index and then it remained stationary. (2) Water which had been in the silica tube for 31 days caused a negligible movement of the index in the opposite direction and again came to rest.

Consider the case in which the water from a glass tube has been introduced into the portion of the tube between *F* and *E*. At a given moment the flow is started.

t Let t be the time measured from the moment of starting;
v v the volume flow in time t;
z z the coefficient of viscosity of the water;
V V half the volume in the manometer between the taps *F* and *E*, that is the total volume flow;
A A the area of the cross-section of the manometer tube.

R The circuit is not of uniform bore; let R denote the value of $(L_1/r_1^4 + L_2/r_2^4)$, where the letters have the obvious meaning.

ρ Let ρ indicate the difference in density between water that has been in the glass tube and pure water.

Then, as is well known in the case of such a circuit, the relation between v and t involves an exponential function of the time, thus

$$v = V(1 - e^{-\rho\lambda t}),$$

λ where λ is a constant. The value of λ in this particular case is $\frac{\pi g}{4ARz}$.

Let $f(v)$ be equal to $\frac{1}{\lambda}\log_e \frac{V}{V-v}$, then it can easily be shown that

$$\rho = f(v)/t.$$

If t be plotted as abscissa and $f(v)$ as ordinate, an approximation to a straight line is obtained, and $\rho = \tan\theta$, where θ is the angle the straight line makes with the abscissa.

Experiments C. (1) The graph, figure 2, shows the result obtained in the experiment of June 8, 1930, when the manometer water had been in the glass tube for 29 days, and where $\rho = 0{\cdot}00013$ gm./cm.^{3} (2) In a second experiment, where the water had been in the glass tube for 7 days only, $\rho = 0{\cdot}000022$ gm./cm.^{3} (3) In a third experiment, where the water had been in the glass tube for 24 days, $\rho = 0{\cdot}000054$ gm./cm.^{3}

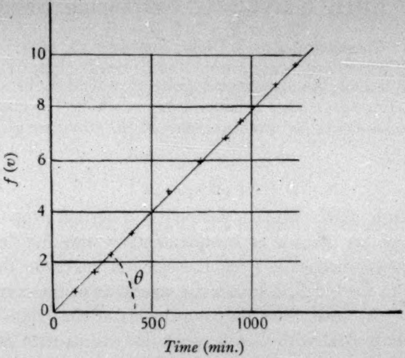


Figure 2.

To save expense, part of the apparatus used for the manometer experiments described in the previous paper was employed. It might be an improvement to increase the diameter of the vertical tubes. In this case the speed of the index would not diminish considerably during the course of an experiment. If one knew the difference between the density of a standard weak solution and that of water, it would not be necessary to know the exact dimensions of the apparatus. The difference in density would be inversely proportional to the time taken for the index to move through a given range.

535.62—291

SOME COMPLEMENTARY COLOUR RELATIONS

By ERIK GENBERG, Norrköping, Sweden

Communicated by J. Guild, September 12, 1933

ABSTRACT. The author has determined pairs of wave-lengths which are complementary with respect to equi-energy radiation taken as white. The energy and luminosity of one of the complementaries for unit luminosity of the white are given.

§ 1

A PAIR of stimuli which, when combined in a certain proportion, are able to match white are known as complementary stimuli. These pairs can be determined geometrically from the spectral curve on the colour triangle or algebraically from the C.I.E. colorimetric standards or the corresponding values in another system. In both cases the coordinates of the white must be known, and it is impossible to deal with complementaries except with regard to a certain selected white.

When we seek to define a standard white, we find that there is nothing to make us prefer one blend of spectral energies to another. A unique white does not exist. Daylight, which we commonly consider as producing a colourless sensation, varies considerably in its properties both in different parts of the world and at different seasons, as well as at different times of the day. The daylight therefore is not a defined blend of spectral energies and cannot be used as an adequate definition of a white light.

The only way to find a standard white is to discard subjective criteria of whiteness and choose a radiation with certain physical properties. The simplest of these radiations is the equi-energy radiation, and in the present paper this hypothetical blend is to be considered as the white, to which the complementary pairs are to be referred.

It must be noted that the sensation produced by an equi-energy radiation does not differ very much from those produced by sources which we commonly consider as white, and therefore no serious objections can be raised against the above choice on the ground that it does not correspond to subjective white.

We can imagine both real and unreal complementaries, but of greatest interest are the complementary relations for the real stimuli of maximum saturation, i.e. the spectral stimuli and the stimuli which lie on the straight line joining the two ends of the spectral curve, i.e. the most saturated purple colours. It is a well-known fact that the spectral stimuli in the middle region of the spectrum have no spectral complementaries, so in order to get a definition applicable throughout the whole spectrum, J. Guild* has proposed to term these pairs *extreme* complementaries.

---

* In a private letter to the author.

We denote a trichromatic unit of white and two complementary stimuli by *W*, *A*, and *B*. Their unit equations we denote as follows: **W, A, B**

$$\left.\begin{aligned} W &= x_0X + y_0Y + z_0Z \\ A &= x_1X + y_1Y + z_1Z \\ B &= x_2X + y_2Y + z_2Z \end{aligned}\right\} \qquad \ldots\ldots(1).$$

X, Y, Z
x, y, z
$1, 2$

In the colour triangle these three colours must lie on the same straight line. As the condition for complementarity we therefore obtain

$$\begin{vmatrix} x_0 & y_0 & z_0 \\ x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \end{vmatrix} = 0 \qquad \ldots\ldots(2).$$

For a system where the white lies in the centre of the colour triangle we get

$$\begin{vmatrix} 1 & 1 & 1 \\ x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \end{vmatrix} = 0 \qquad \ldots\ldots(3)$$

and

$$x_1\frac{3y_2 - 1}{y_2 - x_2} - y_1\frac{3x_2 - 1}{y_2 - x_2} = 1 \qquad \ldots\ldots(3\,a).$$

From this equation we can derive the spectral complementaries shown in the table. For the spectral stimuli, which have no spectral complementaries, the extreme complementaries must lie on the straight line joining the two ends of the spectral curve. We denote a trichromatic unit of the two end colours by *M* and *N*, and their unit equations as follows: **M, N**

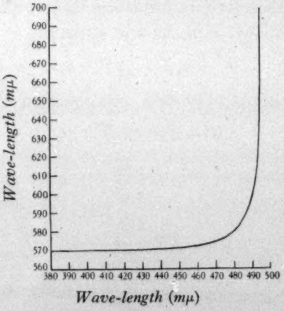


Figure 1. The spectral complementaries in regard to equi-energy-white.

$$\left.\begin{aligned} M &= x'X + y'Y + z'Z \\ N &= x''X + y''Y + z''Z \end{aligned}\right\} \qquad \ldots\ldots(4).$$

$'$, $''$

If the colour A lies on this line, its co-ordinates must satisfy the equation

$$\begin{vmatrix} x_1 & y_1 & z_1 \\ x' & y' & z' \\ x'' & y'' & z'' \end{vmatrix} = \begin{vmatrix} x_1 & y_1 & 1 \\ x' & y' & 1 \\ x'' & y'' & 1 \end{vmatrix} = 0 \qquad \text{......(5),}$$

$$y_1 - y' = \frac{y'' - y'}{x'' - x'}(x_1 - x') \qquad \text{......(5 a).}$$

In the C.I.E. system we obtain

$$\left.\begin{aligned} \lambda' &= 700 & \lambda'' &= 380 \\ x' &= 0{\cdot}7347 & x'' &= 0{\cdot}1741 \\ y' &= 0{\cdot}2653 & y'' &= 0{\cdot}0050 \end{aligned}\right\} \qquad \text{......(6),}$$

(5, 6) $$y_1 = 0{\cdot}4643 \quad x_1 - 0{\cdot}0758 \qquad \text{......(7).}$$

We now derive

(3, 7) $$x_1 = \frac{(y_2 - 1{\cdot}2274)\,(x_2 + 0{\cdot}0758)}{(3y_2 - 1{\cdot}3929)\,(x_2 - 0{\cdot}5357)} \qquad \text{......(8).}$$

From the equations (7) and (8) we can calculate the co-ordinates for the extreme complementaries which are non-spectral stimuli. These also are shown in the table.

§ 2

We shall now calculate the quantities of the complementaries which are necessary to match the white, and therefore we transform its co-ordinates to the system ABC,

C where C is an arbitrary colour with the unit equation

3 $$C = x_3 X + y_3 Y + z_3 Z \qquad \text{......(9).}$$

A and B are defined above. The new unit equation for white we write

a, b, c $$W = aA + bB + cC \qquad \text{......(10)}$$

and obtain

$$\left.\begin{aligned} a &= \frac{1}{3}\frac{D_1}{D} \\ b &= \frac{1}{3}\frac{D_2}{D} \\ c &= \frac{1}{3}\frac{D_3}{D} \end{aligned}\right\} \qquad \text{......(11),}$$

where

D_1 $$D_1 = \begin{vmatrix} 1 & 1 & 1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} \text{ etc.}$$

and

D $$D = \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix}.$$

In regard to the condition for complementarity (3) we obtain

$$\left.\begin{aligned} a &= \frac{1}{3}\frac{1-3x_2}{x_1-x_2} \\ b &= \frac{1}{3}\frac{1-3x_1}{x_2-x_1} \\ c &= 0 \end{aligned}\right\} \quad \ldots\ldots(11\,a),$$

$$a+b=1 \quad \ldots\ldots(12).$$

The luminosities we denote by L and obtain L

$$L_W = aL_A + bL_B \quad \ldots\ldots(13),$$

$$\left.\begin{aligned} L_A &= x_1L_x + y_1L_y + z_1L_z \\ L_B &= x_2L_x + y_2L_y + z_2L_z \end{aligned}\right\} \quad \ldots\ldots(14),$$

(11 *a*, 13, 14) $$L_W = \tfrac{1}{3}(L_x + L_y + L_z) \quad \ldots\ldots(13\,a).$$

The luminosity of that quantity of the colour A, which with its complementary colour B matches a white colour of unit luminosity, we denote by L_a and get

$$L_a = \frac{aL_A}{L_W} = \frac{1-3x_2}{x_1-x_2}\,\frac{L_A}{L_x+L_y+L_z} \quad \ldots\ldots(15).$$

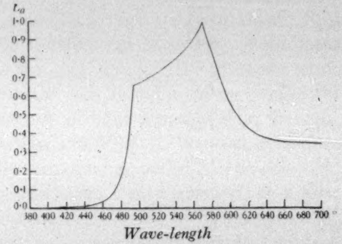


Figure 2. Luminosity values for spectral stimuli matching equi-energy white of unit luminosity with their extreme complementaries.

In the C.I.E. system

$$\left.\begin{aligned} L_x &= 0 \\ L_y &= 1 \\ L_z &= 0 \end{aligned}\right\} \quad \ldots\ldots(16),$$

(15, 16) $$L_a = y_1\frac{1-3x_2}{x_1-x_2} \quad \ldots\ldots(15\,a).$$

If the standard visibility function is denoted by V, the energy which corresponds to the luminosity L_a is expressed, in arbitrary units, by V

$$E_a = L_a/V_A \quad \ldots\ldots(17).$$

From equations (15 *a*) and (17) the luminosity and energy values shown in the table are calculated.

Table. The complementary colours which for a 1931 C.I.E.-standard observer are chromatically equivalent to an equi-energy radiation of unit luminosity

λ_a	L_a	E_a	λ_b		
700	0·344	84	493·9		
690	0·345	42	493·9		
680	0·346	20·4	493·9		
670	0·348	10·9	493·8		
660	0·352	5·77	493·7		
650	0·359	5·36	493·6		
640	0·371	2·12	493·5		
630	0·391	1·47	493·2		
620	0·421	1·10	492·6		
610	0·472	0·94	491·7		
600	0·553	0·88	490·0		
590	0·675	0·89	486·8		
580	0·836	0·96	479·6		
570	0·992	1·04	427·3		
			x	y	z
560	0·903	0·91	0·2963	0·0618	0·6419
550	0·840	0·84	0·3549	0·0890	0·5561
540	0·796	0·83	0·3896	0·1051	0·5053
530	0·759	0·88	0·4151	0·1169	0·4680
520	0·727	1·02	0·4395	0·1283	0·4322
510	0·699	1·39	0·4771	0·1457	0·3772
500	0·673	2·08	0·5656	0·1868	0·2476
			λ_b		
490	0·447	4·05	600·0		
480	0·171	2·32	580·4		
470	0·071	1·46	574·8		
460	0·036	1·12	572·4		
450	0·021	1·06	571·3		
440	0·013	1·08	570·5		
430	0·008	1·36	570·1		
420	0·006	2·92	569·9		
410	0·006	9·1	569·8		
400	0·006	27·4	569·7		
390	0·006	93·0	569·7		
380	0·006	286	569·7		

OBITUARY NOTICES

EDWIN EDSER, A.R.C.Sc., F.Inst.P.

Edwin Edser, who died on August 17, 1932, will be remembered as an inspiring colleague by many who at some time had the privilege of working with him, and as a clear exponent in many branches of physics by the much larger body who used his text-books. He always brought original ideas to the solution of any problem, and although he was best known as an experimentalist, he was no mean mathematician. In his text-books he always avoided the use of the differential and integral calculus but, as he said, a use of the calculus often evades the real understanding of the problem, and anyone familiar with the methods of the calculus can abbreviate the proofs he gave by employing the symbolic method.

Edser completed his days as a student at the Royal College of Science in 1892 by taking the Associateship of that College, but at this early date he exhibited his originality and experimental ability by devising in conjunction with Herbert Stansfield a portable instrument for measuring magnetic fields* which shows a care in the detail of construction not always attained. From 1892 to 1895 Edser was a demonstrator in the physical laboratory of the Royal College of Science, and during this time his chief interest lay in constructing an efficient form of Michelson's interferometer with the view of measuring the effect of the motion of water upon the velocity of light propagated in the direction of movement of the water. In conjunction with Prof. A. W. Rücker he showed that the combination tones produced by two sounding bodies had an objective existence†. Attaching one of the mirrors of Michelson's interferometer to a fork of pitch equal to the required combination tone, he showed by the disappearance of the fringes that the fork was resounding and consequently that the tone had an objective existence and was not a subjective effect.

From 1895 to 1903 Edser was in charge of the teaching of physics in the South-Western Polytechnic, Chelsea, and during this time he published, with C. P. Butler, the simple method of calibrating prismatic spectra which still goes by his name‡. Two reflecting surfaces at a small angle, such as two pieces of plate glass, are placed in front of the slit of the spectroscope. The spectrum is then crossed by a number of light and dark hands which form a wave-length scale, so that if any two lines of known wave-length are present, the other lines can be determined to within 0·4 tenth-metre. At this time too he found one of those gaps in classical theory which, as he said, he had always looked for but never hoped to find. This is indicated in the title of his paper to the Royal Society "An extension of Maxwell's electromagnetic theory of light to include dispersion, metallic reflection and allied phenomena"*. Treating a dielectric as consisting, like an electrolyte, of molecules having two oppositely charged atoms, we have in the simplest case, in a field P,

---

* *Phil. Mag.* **34**, 186 (1892).

† *Proc. Phys. Soc.* **13**, 412 (1895).

‡ *Phil. Mag.* **46**, 207 (1898).

$$P(1 + 4\pi M) = 4\pi D,$$

where $1 + 4\pi M$ represents the dielectric constant. Maxwell's first equation is unchanged, but the second equation is modified by adding $\Sigma q v_x$ to the displacement current, where q is the atomic charge and v_x the velocity of that charge. Subsidiary equations for atomic vibrations (rotational and separational) are given, and finally

$$\mu^2 = \mu_\alpha + \frac{c'\lambda^2}{\lambda^2 - \lambda_1^2} + \frac{c''\lambda_2^2}{\lambda^2 - \lambda_2^2},$$

which is the most general form of Ketteler's dispersion formula. Double refraction in uniaxal crystals is discussed, an extension is made by introducing a viscous term, and the ordinary laws of metallic reflection as given by Cauchy are deduced. His treatment is an improvement on Helmholtz's theory, as a more definite physical significance is given to the constants introduced.

From 1903 to 1914 Edser was Head of the Department of Physics at the Goldsmith's College, and took considerable part in the academic work of the University of London. In 1914 he published a paper on "The reflexion of electromagnetic waves at the surface of a moving mirror"†. By showing that a unit charge in the conducting mirror is subject not only to the electric fields of the incident and reflected waves but also to a force in their magnetic fields due to its own motion with the mirror, he proved that the amplitude of the reflected wave is not the same as that of the incident wave. The case of oblique incidence also was treated.

From 1915 Edser devoted himself to the work of Minerals Separation, Ltd. and here his interest in the subject of surface tension proved of immense value. His two articles in the *Reports on Colloidal Chemistry* of the British Association are of importance in the metallurgical processes concerned, but above all make a valuable and fascinating addition to the literature on the subject. The first article on "Molecular attraction and the physical properties of liquids"‡ comprises in the first place a review of the possible laws of attraction which account for the facts of surface tension, intrinsic pressure, and cohesion, giving in historical order the methods of Laplace, Rayleigh and others. Then, assuming that attraction $\propto r^{-n}$, he calculates the cohesion by two independent methods: first directly from the definition of cohesion by integration, across an imaginary plane, of the forces due to the individual molecules on opposite sides of it; and secondly from the expression for cohesion extracted from the virial equation of Clausius. The two methods give identical results. n must be greater than 4 for cohesion to exist at all. Surface tension is then calculated by Gauss's method and it becomes obvious that for surface tension to exist at all n must be greater than 5. From the surface tension of very small bubbles and drops it appears that n must be greater than 7.

---

* *Proc. R.S.* **63**, 91 (1898).

† *Phil. Mag.* **28**, 508 (1914).

‡ *Fourth Report Coll. Chem. Brit. Assoc.* p. 40 (1922).

Probably $n = 8$. No assumptions are made as to the structure of the molecule. Two further conclusions are aimed at, namely that the energy of surface tension exists to the extent of 94 per cent in a layer one molecule thick, and that at a depth equal to a molecular diameter the intrinsic pressure is 8·5 per cent less than the maximum value in the interior of the liquid. Tables of surface density calculated from latent heats for 65 substances show sufficient agreement with the experimental values to bear out the validity of the work, and a similar agreement exists in the case of 84 substances in which it is calculated from the density and thermal expansibility. The remaining paper* on "The concentration of minerals by flotation" describes the flotation of heavy bodies on liquids and its applications in separating floatable materials such as galena and blende from non-floatable materials such as quartz. A heavy body which floats upon a liquid is supported by the surface tension of the liquid and by the hydrostatic pressure of the liquid below it; the former predominates for small bodies and the latter for large ones. The adhesion to bubbles in a froth has a similar cause and the methods of producing flocculation and deflocculation are described and discussed. Flocculation is explained in terms of the angle of contact between the air-liquid surface and the liquid-solid interface owing to the repulsion of the water from between the particles and the consequent moving together of the particles as though attraction existed. The particles that can be flocculated are exactly those that can float on a liquid less dense than themselves.

Every branch of physics touched by Edser was elucidated by his active mind, and although his work was not all well known it was all of high intrinsic merit.

S. G. STARLING

---

* *Fourth Report Coll. Chem. Brit. Assoc.* p. 263.

SIR RICHARD THRELFALL

WITH the passing of Sir Richard Threlfall in July 1932 a gap was left in the ranks of men of science which, in these days of specialization, it will be hard to fill, for Sir Richard was many-sided in his interests and yet no dilettante. He spoke with knowledge and authority among chemists, physicists, and mechanical or electrical engineers, and was keenly interested in horticulture and entomology. Once his interest in a problem was aroused, no matter what the subject, he would attack it scientifically, and continue the attack from all sides until he could see clearly the way to a solution. By training and inclination he was a physicist, and spoke of himself as a "chemist by adoption": nevertheless it was to Sir Richard Threlfall that the Society of Chemical Industry in 1929 awarded its medal—the blue riband of the profession of applied chemistry.

He used to relate how, as a boy, he learnt all the tricks of the trade that the village blacksmith could teach him, and spent his pocket-money on materials for experiments, making most of his own apparatus. To the end of his life he preferred the old type of Bunsen burner to the more modern adaptations of it. His book *Laboratory Arts* (Macmillan), first published in 1898, was no scissors-and-paste compilation; it was obviously written by one who had himself used the methods there described, many of which were original.

Of the twenty or so various researches, the results of which he published during the period 1886–1899, many have a distinct bearing on pure chemistry. From his early association with Prof. J. J. Thomson in researches on the effect produced by the passage of electric discharge through pure nitrogen and on the production of ozone he was led to study the electrical properties of pure substances; in the *Philosophical Magazine* for 1893 he describes the preparation of pure nitrogen and attempts to condense it, and in the *Philosophical Transactions* for 1894 he describes the electrical properties of pure sulphur.

It was during his residence in Sydney (1886–1899) as Professor of Physics at the University that Threlfall became interested in the study of fuels from the chemical as well as the physical point of view, and he was appointed President of the First and Second New South Wales Royal Commission on the spontaneous combustion of coal cargoes. His interest in fuel problems and the economic generation of power found scope at a later date when in 1899 he joined the firm of Messrs Albright and Wilson, Ltd., of Oldbury, Birmingham. Here he devoted himself to the direction of researches bearing on the application of engineering, and particularly electrical engineering, to chemical manufacture. The generation of producer gas and its distribution early claimed his attention, and formed the subject of a paper read to the Society of Chemical Industry in 1907. The methods then used for the metering of large volumes of producer gas were far from satisfactory, on account of interference due to deposition of tar in the mains. Threlfall selected the Pitot-tube method as the most suitable and, after a careful study of the factors involved, incorporated it in a continuous recording instrument, which he described before the Institution of Mechanical Engineers in 1904.

Sir Richard Threlfall's intimate knowledge not only of fuel problems but also of the requirements of industries depending upon the economic utilization of our fuel supplies led to his appointment as Chairman of the Fuel Research Board in succession to Sir George Beilby.

As Technical Director of Messrs Albright and Wilson, Ltd., which post he held until shortly before his death, he undertook the investigation of electrochemical methods for the commercial production more particularly of potassium chlorate, ammonium persulphate and electrolytic zinc. Many of his noteworthy achievements in this connection are necessarily as yet unpublished. They are triumphs of chemical engineering. As early as 1894, when resident in Australia, he had been interested in the zinc workings at Broken Hill and had recognized the potentialities of pure electrolytic zinc, but it was not until nearly fifteen years later that the commercial production of pure zinc became attractive. Threlfall courageously decided to manufacture from fused zinc chloride. The economic production of zinc chloride and its dehydration on a large scale in such a way as to avoid the formation of the oxychloride had not hitherto been achieved. A full description of the process, together with the still more original methods used for electrolysis of the fused chloride, is to be found in the *Transactions of the Society of Chemical Industry* for 1929. On reading the account of this work one is struck with the tenacity and perseverance shown in overcoming almost insuperable difficulties in the use of unusual materials of construction. The more difficult the problem experimentally, the more it appealed to Threlfall—his interest was "where the cackle ends and where the 'osses begin."

During the War his services were enlisted on the Trench Warfare Committee, and subsequently on the Board of Invention and Research and the Chemical Warfare Committee. In this capacity he was instrumental in initiating many lines of activity. He was early recognized as an authority on the production of smoke screens and bombs. Jointly with Sir William Ramsay he was the first to explore the possibility of developing supplies of helium for use in airships within the Empire, and in his own laboratory he carried out many experiments on the production and safe handling of hydrogen.

As Chairman of the Chemistry Co-ordination Research Board, Threlfall saw clearly the need and scope for a national research institution, and chemists owe to him more than to any other the foundation of the Chemical Research Laboratories at Teddington—a fitting monument to a life spent in the service of technical chemistry.

G. KING

SIR RICHARD THRELFALL, the experimentalist

Sir Richard Threlfall was essentially a skilled experimentalist ready to embark on any difficult investigation that interested him, and it may be said that the more difficult it was the more he revelled in it. In all he did his strong personality asserted itself.

The variety of laboratory operations which he had practised is illustrated in his book *On Laboratory Arts* (1898) which, like Shenstone's book on glass-blowing, bears on every page clear evidence of personal attention to detail. Detail is hardly the word; I mean the minutest detail in an operation which is important in facilitating its practice or in ensuring success. Those who are not themselves skilled experimenters, that is those who do not do things but merely talk or write or calculate about things done by others, may not appreciate how much there is in such detail. Threlfall in his book emphasized this, for he said he had not, except where he had specifically stated the contrary, described any operation which he had not practised himself, and he might have added "in which he was not also an adept."

His manipulative skill was great and the fact that he had lost several fingers from too incautious experiment with nitro-explosives did not deter him from his beloved laboratory pursuits.

It seems to me a sad reflection that his book on laboratory arts should so long have remained out of print. A new edition was badly needed and in his last years he was, it seemed to me, rather half-heartedly preparing for a new edition. It is to be hoped that someone who is equally skilled and who is familiar with the multitude of modern laboratory operations at first hand may be induced to carry on where Threlfall left off, and complete a new edition.

Threlfall's exceptional personality must have been a surprise to the University authorities at Sydney when he first arrived as the newly appointed professor of physics. He found they had nothing at all in the way of laboratory or equipment. No doubt there was a blackboard. Threlfall demanded instantly that tools and apparatus of which he presented a list should be provided. This was an uncontemplated, and no doubt some thought it an unnecessary, expense, and when they seemed disinclined to meet his wishes in the matter he answered "I am going back to England by the next ship." He got all he wanted. I regret that I cannot refer to any document to confirm this story. It is just as I remember it from his own lips. It may in detail be not exactly right but substantially it is.

From his book, of which I am glad to own a presentation copy, it will be seen how thoroughly he pursued and how far he advanced in a number of difficult laboratory arts. His glass-blowing was quite exceptional for a non-professional, and the casual amateur would do well to notice, merely as one instance of attention to detail, how much trouble and care Threlfall took in cleaning his glass before operating upon it.

It used to be not unusual to find amateurs who make their own telescope mirrors, and some really excellent mirrors have so been made. It is sufficient to mention A. A. Common, who started as an amateur. Threlfall, however, went further and made an acromatic telescope objective and other lenses. This was before the days of the triple objective, so we find the ordinary acromatic pair of flint and crown.

Among the laboratory operations described in detail by Threlfall was one which more particularly interests me, that of making quartz fibres. These attracted much attention in this country when I first showed them in 1887, but I do not remember that anyone here meddled with them until Shenstone, a Master at Clifton College, got interested. Threlfall, however, read about them, and not deterred by the handicap of missing fingers experimented at first unsuccessfully. On reading further accounts he started again and succeeded perfectly. He then found that in describing the perfect elasticity of the fibres I had understated the case and, as he said in the words of the Queen of Sheba, the half had not been told to him. It may be of interest to give what I believe to be the reason for his first want of success, because I experienced this myself for I think two whole days. It is repugnant to anyone who is a glass-blower to try to do any work in the flame, and it must have been as impossible for Threlfall as it was to me to dare to draw the fibres actually in that intensely hot oxyhydrogen flame. I still cannot understand why they do not draw off. Threlfall made use of the extreme perfection of the elasticity to make a gravimeter, but then he found that the fibres had a positive temperature coefficient of rigidity which required very good thermostatic means to counteract it.

In later years Threlfall developed a recording gas calorimeter, and to resist the highly corrosive products of combustion of the Mond gas for which it was made he used pure lead for the combustion chamber. In this I was glad to follow him until I found a better material.

I regret that I am unable to add any observations on his later activities. These have related largely to manufacturing operations, and naturally he did not discuss these outside the works.

C. V. BOYS

REVIEW OF BOOK

Applied X-Rays, by G. C. CLARK. 2nd edition. 470 pp. (McGraw-Hill.) 30*s*. net.

This well-known work has won a niche for itself in the literature of the subject. The second edition is considerably larger than the first and the matter is presented in a more logical order. The book is divided into two parts, the first dealing with general physics and the applications of X-rays, and the second with the X-ray analysis of the ultimate structures of materials.

The book has been largely re-written except for some of the material in the earlier portions. The results of the crystal analysis of elements and compounds are brought up to date and valuable tables of the structures of elements and compounds are included. A useful and concise account is given of the structure of alloys and the attempts which are now being made to explain their properties. This is followed by a summary of recent work on the diffraction of X-rays by liquids and amorphous bodies. Completely new chapters have been written on chemical analysis by X-rays, inorganic crystal chemistry (in which the laws of formation of crystals, types of bonding, co-ordination in crystals, etc. are discussed according to recent notions) and the structure of highly polymerized organic substances found in nature.

The author has endeavoured to supply sufficient theoretical framework to elucidate the interpretation of the results obtained by X-ray methods, but the theoretical explanations suffer in general from too much compression. This is especially noticeable in the account of the determination of atomic arrangement from intensity data.

We have noted a few omissions and inaccuracies. The two photographs of single crystals of sapphire on p. 352 are incorrectly described as Laue patterns, and it is a little surprising to find in the section dealing with fibre-structure no indication of any methods other than trial and error, and that no reference is made to the pole-figures of Wever, upon which so much of the best work depends.

The book bears evidence of an attempt to cater for the intelligent inquirer and at the same time to satisfy the experimentalist, and on the whole the attempt is successful. An immense amount of information is contained in it, and it will no doubt continue to be used by those who are interested in the subject of applied X-rays.

INDEX

PAGE

Absolute measurement of electrical resistance in terms of inductance and frequency 545
Air in pipes, An investigation into the flow of 91
Air screw, Intensity of low-frequency sounds close to 727
Aniline and benzene, A determination of the specific heats of 194
Appleton, E. V.: On two methods of ionospheric investigation 673
Appleton, E. V. and Builder, Geoffrey: The ionosphere as a doubly refracting medium 208
Appleton, E. V. and Naismith, R.: Weekly measurements of upper-atmospheric ionization 389
Atmospheric ionization, Weekly measurements of upper 389
Atmospheric ions, Relations between the combination coefficients of 367

Balls, E. G., *see* Nettleton, H. R.
Band, William, *see* Chang, W. Y.
Bates, L. F.: A new apparatus for the measurement of the earth's magnetic field 180
Bates, L. F. and Lloyd-Evans, B. J.: A compact electromagnet for general purposes 425
Beach, A. C. G.: An experiment bearing on Talbot's bands 474
Beck, W. L.: A new capacity-meter 765
Bell, Mary and Green, S. E.: On radiometer action and the pressure of radiation 320
Benzene, A determination of the specific heats of aniline and 194
Blatchford, A. H.: The diffraction of X-rays by liquid sulphur 493
Boron monoxide, The intensities of bands in the spectrum of 627
Bradley, A. J. and Jay, A. H.: Quartz as a standard for accurate lattice-spacing measurements 507
Brown, E.: The demonstration of eddy currents in conductors of various shapes 555
Builder, Geoffrey, *see* Appleton, E. V.

Cadmium, Hyperfine structure in the spark spectrum of 625
Camera for precision measurements, A high-temperature X-ray 635
Campbell, N. R.: The measurement of visual sensations 565
Capacity-meter, A new 765
Carbon dioxide, Vibrations produced in bodies by contact with 101
Cathode-ray oscillogram, Time marking a 135
Chang, W. Y. and Band, William: Thermomagnetic hysteresis in steel 602
Clock, A new type of free-pendulum 41
Colour relations, Some complementary 836
Complementary colour relations, Some 836
Conductivities of rocks, A method for the determination of thermal 447
Conductivity of water, The thermal 523
Conductors, A method of measuring the specific heats of poor 591
Connelly, F. C.: The band spectrum of tin oxide 780
Crystalline state of thin spluttered films of platinum 381

PAGE
Demonstrations 482, 741
Density of a liquid, Determining a small change in the 833
Diatomic rotator with two degrees of freedom, A model to illustrate the motion of a 266
Discharge characteristics, The control of ignition-coil 288
Discharge in gases at normal temperatures and pressures, An experimental study of electrical 20
Duddell Medal, 1933, Presentation of the 742

Earth's electric field, The influence of atmospheric suspensoids upon the . . 152
Earth's magnetic field, A new apparatus for the measurement of the . . . 180
Echelons for the visible and ultra-violet regions, The construction, testing and use of reflection 699
Eddington, Sir A. S.: Notes on the method of least squares 271
Eddy currents in conductors of various shapes, The demonstration of . . 555
Edser, Edwin, Obituary notice of 841
Elastic constants of rocks, with a seismic application 70
Electro-endosmosis and electrolytic water-transport 755
Electromagnet for general purposes, A compact 425
Electromagnetic waves through an ionized medium in the presence of an external magnetic field, The Appleton-Hartree formula and dispersion curves for the propagation of 245
Electrometer, A sensitivity-control for the Lindemann 117
Elliott, A.: The intensities of bands in the spectrum of boron monoxide . . 627

Fabrics, The transmission of heat through 414
Fahmy, M.: A further point of analogy between the equations of the quantum theory and Maxwell's equations 67
Ferguson, Allan and Miller, J. T.: A method for the determination of the specific heats of liquids, and a determination of the specific heats of aniline and benzene 194
Films of platinum, The crystalline state of thin spluttered 381
Finch, G. I. and Sutton, R. W.: The control of ignition-coil discharge characteristics 288
Flow of air in pipes, An investigation into the 91
Flow of liquid suspensions, The 142
Floyd, W. F.: A note on interference tones in superheterodyne receivers . . 610
Fluorescent screens, The spurious ring exhibited by 434
Frequency-change and group-retardation methods of measuring ionized-layer equivalent heights, A comparison of the 235

Gases at normal temperatures and pressures, An experimental study of electrical discharge in 20
Genberg, Erik: Some complementary colour relations 836
Geophysical stations by the method of least squares, The rapid adjustment of observations in a network of 792
Green, S. E., *see* Bell, Mary
Grimmett, L. G.: A sensitivity-control for the Lindemann electrometer . . 117
Group-retardation methods of measuring ionized-layer equivalent heights, A comparison of the frequency-change and 235

PAGE
Hampton, W. M.: The visibility of objects in a searchlight beam 663
Heard, J. F.: Pressure effects in the spectra Xe I and Xe II 734
Heat through fabrics, The transmission of 414
Hepburn, H. C.: Electro-endosmosis and electrolytic water-transport . . 755
Herd, J. F.: The generation and reception of wireless signals of short duration . 221
Hughes, J. V.: The spurious ring exhibited by fluorescent screens . . . 434
Hygrometer, The wet-and-dry-bulb 307

Ice and liquid water, The molecular structure of 768
Ignition-coil discharge characteristics, The control of 288
Induced magnetism, A common misapprehension of the theory of induced . 82
Intensities by means of a microphotometer, The direct recording of relative . 441
Intensities of bands in the spectrum of boron monoxide 627
Interference tones in superheterodyne receivers, A note on 610
Ionization, Weekly measurements of upper-atmospheric 389
Ionized-layer equivalent heights, A comparison of the frequency-change and group-retardation methods of measuring 235
Ionized medium in the presence of an external magnetic field, The Appleton-Hartree formula and dispersion curves for the propagation of electromagnetic waves through an 245
Ionosphere, An automatic recording method for wireless investigations of the 399
Ionosphere as a doubly refracting medium, The 208
Ionospheric investigation, On two methods of 673
Ions, Relations between the combination coefficients of atmospheric . . . 367

Jay, A. H.: A high-temperature X-ray camera for precision measurements . 635
Jay, A. H., *see* Bradley, A. J.
Jones, E. Gwynne: Hyperfine structure in the spark spectrum of cadmium . 625
Jones, E. Gwynne: Hyperfine structure of perturbed series 501
Jones, E. Lancaster: The rapid adjustment of observations in a network of geophysical stations by the method of least squares 792

Kemp, C. F. B.: Observations on the intensity of low-frequency sounds close to a metal air screw 727
Kerr cell, A note on the 469
Kinematic supports and clamps 120
Kinsey, E. L. and Sponsler, O. L.: The molecular structure of ice and liquid water 768

Lang, K. C., *see* Martin, L. H.
Lattice-spacing measurements, Quartz as a standard for accurate . . . 507
Least squares, Notes on the method of 271
Least squares, The rapid adjustment of observations in a network of geophysical stations by the method of 792
Lindemann electrometer, A sensitivity-control for the 117
Liquid, Determining a small change in the density of a 833
Liquids in the ultra-violet region, A new apparatus for rapid spectrophotometry of 1
Lloyd-Evans, B. and Watts, S. S.: An investigation into the flow of air in pipes 91
Lloyd-Evans, B. J., *see* Bates, L. F.
Lothian, G. F., *see* Twyman, F.

PAGE
Magnetic field, A new apparatus for the measurement of the earth's 180
Magnetism, A common misapprehension of the theory of induced 82
Manometer due to Prof. A. Griffiths, A study of a sensitive 808
Marley, W. G.: A method of measuring the specific heats of poor conductors . 591
Marsh, M. C.: The transmission of heat through fabrics 414
Martin, L. H. and Lang, K. C.: The thermal conductivity of water 523
Maxwell's equations, A further point of analogy between the equations of the quantum theory and 67
Metal by means of an oscillating disc, The measurement of the viscosity of a molten 530
Metals, A photographic method of deriving the optical constants of the . . 49
Microphotometer, The direct recording of relative intensities by means of a . 441
Miller, J. T., *see* Ferguson, Allan
Murison, C. A., *see* Thomson, G. P.

Naismith, R.: A comparison of the frequency-change and group-retardation methods of measuring ionized-layer equivalent heights 235
Naismith, R., *see* Appleton, E. V.
Nancarrow, H. A.: A method for the determination of the thermal conductivities of rocks 447
Nancarrow, H. A.: Tables to facilitate the calculation of the temperature-distribution in a cylinder 462
Nettleton, H. R. and Balls, E. G.: Two simple methods of absolute measurement of electrical resistance in terms of inductance and frequency 545

Optical constants of the metals, A photographic method of deriving the . . 49
Oscillogram, Time-marking a cathode-ray 135

Perturbed series, The hyperfine structure of 501
Pressure effects in the spectra Xe I and Xe II 734

Quantum theory and Maxwell's equations, A further point of analogy between the equations of the 67
Quartz as a standard for accurate lattice-spacing measurements 507

Radiation, On radiometer action and the pressure of 320
Radiometer action and the pressure of radiation, On 320
Ratcliffe, J. A. and White, E. L. C.: An automatic recording method for wireless investigations of the ionosphere 399
Reflection echelons for the visible and ultra-violet regions, The construction, testing and use of 699
Refracting medium, The ionosphere as a doubly 208
Resistance in terms of inductance and frequency, Two simple methods of absolute measurement of electrical 545
Reviews of books 126, 358, 485, 617, 745, 848
Richards, T. C.: On the elastic constants of rocks, with a seismic application . 70
Richardson, E. G. and Tyler, E.: The flow of liquid suspensoids 142
Richardson, Lewis F.: Time-marking a cathode-ray oscillogram 135
Ring exhibited by fluorescent screens, The spurious 434
Rocks, A method for the determination of the thermal conductivities of . . 447
Rocks, The elastic constants of 70
Rotator with two degrees of freedom, A model to illustrate the motion of a diatomic 266

PAGE

Searchlight beam, The visibility of objects in a 663
Sensations, The measurement of visual 565
Siegbahn, M.: Studies in the extreme ultra-violet and the very soft X-ray region 689
Silver, The absence of fine structure in the arc spectrum of 559
Simons, Lewis and Smart, E. H.: A model to illustrate the motion of a diatomic rotator with two degrees of freedom 266
Smart, E. H., *see* Simons, Lewis
Sounds close to a metal air screw, Observations on the intensity of low-frequency 727
Specific heats of liquids, A method for the determination of the 194
Specific heats of poor conductors, A method of measuring the 591
Spectrophotometry, Conditions for securing accuracy in 643
Spectrophotometry of liquids in the ultra-violet region, A new apparatus for rapid 1
Spectrum analysis 1, 441, 501, 625, 627, 643, 734, 780
Sponsler, O. L., *see* Kinsey, E. L.
Squares, Notes on the method of least 271
Squares, The rapid adjustment of observations in a network of geophysical stations by the method of least 792
Steel, Thermomagnetic hysteresis in 602
Stephenson, J. D.: An experimental study of electrical discharge in gases at normal temperatures and pressures 20
Stott, Vaughan H.: The measurement of the viscosity of a molten metal by means of an oscillating disc 530
Structure in the arc spectrum of silver, The absence of fine 559
Structure in the spark spectrum of cadmium, Hyperfine 625
Structure of ice and liquid water, The molecular 768
Structure of perturbed series, The hyperfine 501
Stuart, Norman, *see* Thomson, G. P. 381
Sulphur, The diffraction of X-rays by liquid 493
Superheterodyne receivers, A note on interference tones in 610
Surface tension, The measurement of 88
Suspensions, The flow of liquid 142
Suspensoids upon the earth's electric field, The influence of atmospheric 152
Sutton, R. W., *see* Finch, G. I.
Sutton, T. Carlton: The measurement of surface tension 88

Talbot's bands, An experiment bearing on 474
Taylor, Mary: The Appleton-Hartree formula and dispersion curves for the propagation of electromagnetic waves through an ionized medium in the presence of an external magnetic field 245
Temperature coefficient of the saturated Weston cell, The 172
Temperature-distribution in a cylinder, Tables to facilitate the calculation of the 462
Tension, The measurement of surface 88
Thermal conductivities of rocks, A method for the determination of the 447
Thermal conductivity of water, The 523
Thermomagnetic hysteresis in steel 602
Thompson, N.: The direct recording of relative intensities by means of a microphotometer 441
Thomson, G. P., Stuart, Norman and Murison, C. A.: The crystalline state of thin spluttered films of platinum 381

PAGE
Threlfall, Sir Richard, Obituary notices of 844
Tin oxide, The band spectrum of 780
Tolansky, S.: The absence of fine structure in the arc spectrum of silver . . 559
Tomlinson, G. A.: A new type of free-pendulum clock 41
Twyman, F.: A new apparatus for rapid spectrophotometry of liquids in the ultra-violet region 1
Twyman, F. and Lothian, G. F.: Conditions for securing accuracy in spectrophotometry 643
Tyler, E., *see* Richardson, E. G.

Ultra-violet and the very soft X-ray region, Studies in the extreme . . . 689

Vibrations produced in bodies by contact with solid carbon dioxide . . . 101
Vigoureux, P. and Watts, S.: The temperature coefficient of the saturated Weston cell 172
Vincent, P. C.: An application of a new method, due to Prof. A. Griffiths, of determining a small change in the density of a liquid 833
Vincent, P. C.: A study of a sensitive manometer due to Prof. A. Griffiths . 808
Viscosity of a molten metal by means of an oscillating disc, The measurement of the 530
Visibility of objects in a searchlight beam, The 663

Waller, Mary D.: Vibrations produced in bodies by contact with solid carbon dioxide 101
Water, The molecular structure of ice and liquid 768
Water-transport, Electro-endosmosis and electrolytic 755
Watts, S., *see* Vigoureux, P.
Watts, S. S., *see* Lloyd-Evans, B.
Weston cell, The temperature coefficient of the saturated 172
Wet-and-dry-bulb hygrometer 307
Whipple, F. J. W.: Relations between the combination coefficients of atmospheric ions 367
Whipple, F. J. W.: The wet-and-dry-bulb hygrometer; the relation to theory of the experimental researches of Awbery and Griffiths 307
White, E. L. C., *see* Ratcliffe, J. A.
Wilberforce, L. R.: A common misapprehension of the theory of induced magnetism 82
Wilberforce, L. R.: Kinematic supports and clamps 120
Williams, S. E.: A photographic method of deriving the optical constants of the metals 49
Williams, W. Ewart: Studies in interferometry—II. The construction, testing and use of reflection echelons for the visible and ultra-violet regions . . 699
Wireless investigations of the ionosphere, An automatic recording method for 399
Wireless signals of short duration, The generation and reception of . . . 221
Wright, E. E.: A note on the Kerr cell 469
Wright, H. L.: The influence of atmospheric suspensoids upon the earth's electric field as indicated by observations at Kew Observatory . . . 152

Xe I and Xe II, Pressure effects in the spectra 734
X-ray camera for precision measurements, A high-temperature 635
X-ray region, Studies in the extreme ultra-violet and the very soft . . . 689
X-rays by liquid sulphur, The diffraction of 493

CAMBRIDGE: PRINTED BY WALTER LEWIS, M.A. AT THE UNIVERSITY PRESS